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Modeling of Alkali Surfactant Polymer Process by Coupling a Multi-purpose Simulator to the Chemistry Package PHREEQC

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SUMMARY

Accurate modeling of an Alkali Surfactant Polymer (ASP) flood requires detailed representation of the geochemistry and, if natural acids are present, the saponification process. Geochemistry and saponification affect the propagation of the injected chemicals and the amount of generated natural soaps. These in turn determine the chemical phase behavior and hence the effectiveness of the ASP process.

In this paper it is shown that by coupling the Shell in-house simulator MoReS with PHREEQC a robust and flexible tool has been developed to model ASP floods. PHREEQC is used as the chemical reaction engine, which determines the equilibrium state of the chemical processes modeled. MoReS models the impact of the chemicals on the flow properties, solves the flow equations and transports the chemicals. The validity of the approach is confirmed by benchmarking the results with the ASP module of the UTCHEM simulator (UT Austin). Moreover, ASP core floods have been matched with the new tool. The advantages of using PHREEQC as the chemical engine are its rich database of chemical species and its flexibility to change the chemical processes to be modeled. Therefore, the coupling procedure presented in this paper can also be extended to other chemical-EOR methods.

1. Introduction

During primary and secondary recovery, as a result of interplay between gravity, viscous, and capillary forces, oil remains trapped in the reservoir pore structure. The remaining oil saturation in the reservoir is a function of the capillary number (Bedrikovetsky, 1993; Lake, 1989): the higher the capillary number the lower the remaining oil. The capillary number is usually defined as

$$N_c = \frac{u\mu}{\sigma} \quad , \quad (1)$$

where u is the Darcy velocity, μ is the viscosity of the displacing fluid, and σ is the interfacial tension (IFT) between the displacing and displaced fluids. The aim of the enhanced oil recovery (EOR) techniques is to decrease the remaining oil saturation by increasing the capillary number. Within realistic field rates this is possible by reducing the interfacial tension. Increasing the viscosity of the displacing fluid mainly affects the macroscopic sweep (mobility control) and does not significantly impact the microscopic sweep.

Alkaline Surfactant Polymer (ASP) flooding is an elegant technology for mobilizing the remaining oil. In this process a slug containing alkaline, surfactant and polymer is injected into the reservoir and chased by a polymer drive. The surfactant lowers the interfacial tension between the oleic and aqueous phases. For crude oils containing natural acids the alkali has a dual purpose: it generates soaps, or natural surfactants, upon reaction with the acid (Johnson, 1972; Caster *et al.*, 1981; deZabala *et al.*, 1982; Ramakrishnan and Wasan, 1983; Porcelli and Binder, 1994) and reduces adsorption of the injected surfactants by inducing a negative charge on the rock surface (Hirasaki and Zhang, 2004). The polymer is added to provide mobility control and to improve the macroscopic sweep.

Designing a successful ASP flood requires finding a suitable mixture of chemicals for the candidate reservoir. For example, alkaline flooding has been studied since 1960's for enhancing oil recovery (Johnson, 1972; Caster *et al.*, 1981). The in-situ generated soap molecules accumulate at the oil-water interface and can considerably reduce the interfacial tension provided that the reservoir conditions, in particular the salinity, are optimal or close to optimal (Nelson, 1982). However, in most reservoirs the salinity of the formation brine is too high, making the alkaline flooding inefficient and uneconomic (Nelson *et al.*, 1984). This problem is solved by addition of a synthetic hydrophilic surfactant in the ASP process. It has been experimentally shown that by adding a small amount of surfactant the optimal salinity of the soap/surfactant mixture can be increased such that "optimal" chemical phase behaviour can be attained under reservoir conditions (Reisberg and Doscher, 1956; Chiu, 1980; Nelson *et al.*, 1984; Rudin and Wasan, 1982; Rudin *et al.*, 1994).

Loss of the injected chemicals, due to the interactions with the rock minerals and other geochemical reactions, is one of the major concerns hindering the application of surfactant-based EOR methods (deZabala *et al.*, 1982; Bunge and Radke, 1983; Mohammadi *et al.*, 2009; Liu *et al.*, 2008; 2010). The loss of chemicals can result in delayed or reduced oil production, scale precipitation or formation plugging problems. The surfactant loss can be considerably reduced by adding alkali to the injected formulation; nevertheless, alkali itself is a reactive component that can be consumed by several reactions in the reservoir. When the crude oil contains natural acids, consumption of alkali by other reactions, delays the saponification reaction. With no sufficient alkali to convert the acid to soap, with presence of surfactant alone, the phase behaviour changes to under-optimum. Therefore, the magnitude of the chemical loss and its effect on the technical and economical efficiency of the process should be evaluated in the ASP models by considering the relevant mechanisms. Ion exchanges between the rock and the cations associated with the alkali, precipitation of carbonate salts, and mineral dissolution are the three main mechanisms that have been considered responsible for the alkali loss in the literature (Cheng, 1986). The cations associated with the surfactant can also be exchanged and affect the surfactant performance.

Field-scale application of alkaline surfactant polymer (ASP) requires detailed understanding of the process. The chemicals are an important part of the costs of an ASP project and thus the economic feasibility of an ASP process should be evaluated through models that could accurately predict the performance of the process in terms of oil production and required amounts of chemicals to be injected. In particular four key features are of interest in such models: (1) in-situ generation of soap (2) the reactions between different species in the aqueous phase and rock minerals, (3) the phase

behavior of the mixture of surfactant, soap, formation and injected water, and oil (4) the lowering of IFT and its effect on incremental oil production (Bhuyan *et al.*, 1990). The details of these features will be discussed in the next section.

UTCHEM is a multi-dimensional chemical flooding compositional simulator that has been developed for research purposes at the University of Texas (UT) in Austin. UTCHEM is generally considered as the reference implementation of soap/surfactant phase behavior, its dependence on other parameters such as salinity or alcohol concentrations, and selected geochemical reactions (Delshad *et al.*, 1996; UTCHEM Technical Documentation, 2000). Different functionalities of UTCHEM have been tested and calibrated by experimental data over the last two decades.

On the other hand, for ASP modeling, the commercial simulators generally focus on the flow and transport properties and do not model the geochemical reactions. Consequently, quantification of the amount of required chemicals and the composition and properties of the produced fluids remain challenging. Recently, Stoll *et al.* (2010, 2011) described a procedure for modeling of the ASP process in a Shell's dynamic reservoir simulator MoReS. The model is based on the work of Liu *et al.* (2008) and uses some features of UTCHEM. It is a two-phase model with an aqueous phase and an oil phase. The properties of the microemulsion phase (during ASP slug injection) and the polymer solution (during injection of polymer) are assigned to the aqueous phase. Some of the key reactions are also incorporated in the model. Numerically, the chemical species are modeled as active components and their flow dynamics are solved explicitly.

Depending on the purpose of the simulations and availability of the experimental data different kinds of models can be used (Karpan *et al.*, 2011). These models range from fractional-flow-theory-based analytical tools to more complex four-phase models including full physical/chemical properties of the process. The primary interest of this study is to develop a tool that can accurately model the geochemistry involved in the chemical EOR processes. We describe an approach that aims to extend the capability of our existing approach for simulating chemically enhanced oil recovery processes. We use the PHREEQC program, developed by Parkurst and Appelo (1999), to calculate the equilibrium concentrations of the chemical species including soap. The flow and transport equations are solved by the dynamic reservoir simulator. The results are benchmarked to UTCHEM. The developed tool can be coupled to any of the ASP models developed in MoReS to simulate the efficiency of the process. The structure of the paper is as follows: Section 2 describes the coupling procedure and details of the implementation of the additional reactions in PHREEQC. In Section 3, we present the results of the coupled model and compare them to the UTCHEM results. In Section 4 we describe the details of the ASP model, whose results are compared to the experimental results in Section 5. We end the paper with concluding remarks.

2. Coupling of PHREEQC and MoReS

To account for the geochemical reactions in subsurface applications, MoReS has been coupled to PHREEQC, which is a software that can simulate the chemical reactions (Parkhurst and Appelo, 1999; Charlton and Parkhurst, 2002). The program provides the equilibrium (and kinetics) chemistry of the *aqueous* solutions interacting with minerals, gases, exchangers, and sorption surfaces (Charlton and Parkhurst, 2002). An advantage of PHREEQC is its extensive database that includes a large number of reactions with their equilibrium reaction constants and enthalpies. It is also possible to extend the database, specify rates for reactions, and add or remove particular reactions.

To solve the coupled flow and equilibration equations, a sequential non-iterative approach (SNIA) has been used (Yeh and Tripathi, 1991). In this method, the flow equations and the chemical-reaction equations are solved separately and sequentially. The coupling procedure is shown in Figure 1. Firstly, the multiphase flow problem is solved and phase saturations and the fluid velocities are obtained. Secondly, these parameters are used for transport of the chemical components. Chemical transport is solved on a component-by-component basis. The advection equation is solved using an higher-order accurate (in time and space) solver to suppress numerical dispersion. For reasons of accuracy and numerical stability, the chemical transport solver makes use of sub-time-stepping. Physical diffusion and dispersion is represented using operator splitting in the advection solver. This chemical transport solver has been used successfully in previous studies to describe fluid (gas-gas) mixing effects and to simulate tracer injection tests. Thirdly, PHREEQC is called to solve the reaction equations, considering each grid block as a single batch reactor. The updated concentrations of the

species are then provided to MoReS to solve the flow and transport equations for the next timestep. Similar to UTCHEM, only a number of primary chemical components are transported in an explicit discretisation scheme. Further details of the coupling procedure can be found in Wei (2010, 2011).

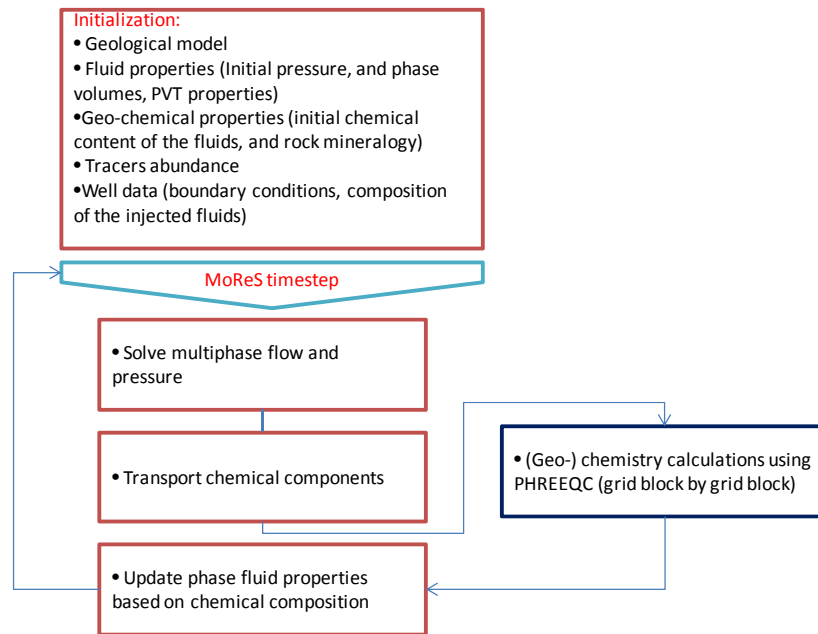


Figure 1: Schematic of the coupling procedure.

2.1. In-situ generation of soap

To describe the oil/alkali chemistry we follow the concept and nomenclature introduced by Bhuyan *et al.* (1990): the pseudo component HA represents the naphthenic acids. The presence of these acids in either the oleic or the aqueous phase is indicated by the subscripts *O* or *W*. Partitioning of the naphthenic acids over the oleic and aqueous phases is described by an equilibrium reaction:



$(HA)_O$ is the moles of the acid in the oleic phase per unit volume of the oil and $(HA)_W$ is the moles of the acid in the aqueous phase per unit volume of water. Although the naphthenic acids in a crude oil may consist of several acid-molecules with different hydrocarbon chain lengths, similar to UTCHEM we model this mixture with a single pseudo-component.

The naphthenic acids present in the aqueous phase can hydrolyse in the presence of alkali to form a water soluble anionic soap A_W^- . The hydrolysis is described by the following reaction and its corresponding equilibrium constant:



The reaction equation shows that the fraction of the acid converted to the soap depends on the pH (Figure 2). Chemically, the soap A_W^- is a water-based component.

The reaction in Eq. (3) can be handled in PHREEQC by introducing a master species A_w and by extending the PHREEQC database with the reaction and the corresponding equilibrium constant. However, PHREEQC only handles reactions in the aqueous phase. Therefore, to represent the partitioning of naphthenic acids between the oleic and aqueous phases in PHREEQC, $[(HA)_O]$, which is expressed in moles per volume of oil (V_O), should be expressed in terms of the water volume (V_W) in the following way:

$$[(HA)_W] = [(HA)_O] \times (V_O / V_W) \quad (4)$$

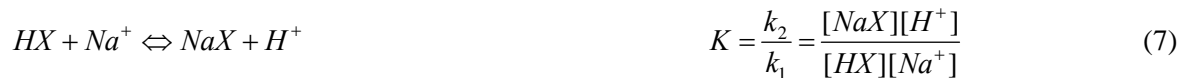
which is defined for non-zero water volume V_w only. In the limiting case of zero water volume, soap formation physically cannot occur and, therefore, this definition does not introduce a model constraint.

2.2. Alkali consumption

Alkali is also consumed in ion exchange processes. To model the ion exchange the amount of the exchanger, represented in the following by the symbol X and defined as master exchange species in the PHREEQC database, should be provided in units of mole per unit mass of water. In principle, multiple exchangers can be defined and the exchanger can have different values in each grid block. By this capability one is able to mimic the heterogeneity in the mineralogy of the reservoir rock. The ion exchange reactions occur in two steps in PHREEQC. For example the hydrogen/sodium exchange is modelled as:



Combination of Eqs. (5) and (6) provides the reaction that is used in UTCHEM for hydrogen/sodium exchange on clays:



Usually values for K are reported in literature while we need to specify k_1 and k_2 in PHREEQC. Equation (7) provides the ratio between these two values. Any pair of numbers whose ratio is K will be suitable for PHREEQC. The same procedure can be followed to determine the equilibrium reaction constants of other exchange reactions.

3. Verification of the approach

This section discusses the results of the described approach. First we confirm the results of the saponification reaction by comparing the implemented reactions in PHREEQC with published experimental data in bulk solutions under static conditions. Afterwards, we include the porous medium (and flow) and benchmark the results against UTCHEM.

3.1. Saponification reaction

To validate the model, we compared our results to the experimental data reported by Rudin and Wasan (1992). Sodium hydroxide (NaOH) was used as alkali in the experiments in a model system that consisted of decane (as oil) and a known amount of sodium oleate (as acid). It was possible to measure the amount of the converted acid, because the acid was insoluble in the oil. With addition of the alkali the acid was converted to soap. Above a certain pH (or alkali concentration) no acid was detectable in the solution meaning that all acid had been converted to soap. The measured data are presented in Figure 2 and compared to the predicted outcome of the implemented reactions in PHREEQC. For the Rudin-Wasan oil-acid system a good agreement between the data and model obtained for $\log K_{eq}^{HAw} = -6.0$. The value of $\log K_{eq}^{HAw} = -4.0$ has been reported by deZabala *et al.* (1982). for a different oil-acid system.

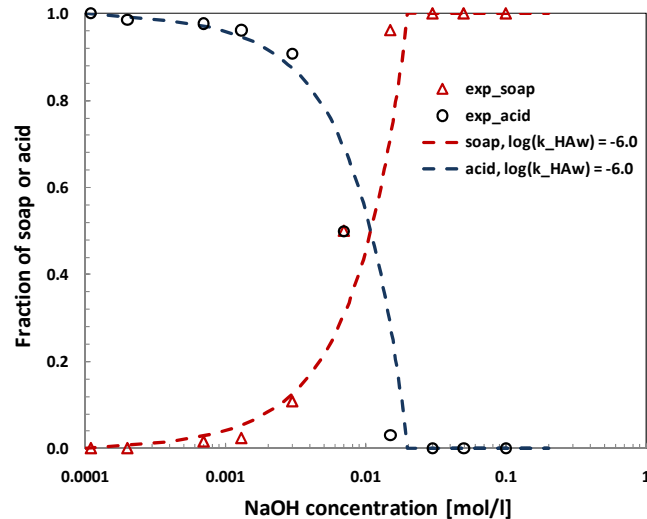


Figure 2: Comparison of experimental data from Rudin and Wasan (1992) with the implemented reactions in PHREEQC with $\log K_{eq}^{HAw} = -6.0$.

3.2. Comparison to the UTCHEM geochemistry module

To verify the performance of the implemented model in porous media, the current model is compared to the UTCHEM results. The comparison is made for a 1D core consisting of 200 equidistant grid blocks. For the following cases our approach was successfully benchmarked against UTCHEM: water flooding, alkaline flooding in a core initially saturated with water (with and without ion exchange reactions), and finally alkaline injection into a core containing oil and water (with and without saponification and cation exchange reactions). The basic properties of the porous medium, the fluids and the injection rates are summarized in Table 1. In this section we will present some of our benchmarking results.

A difference between PHREEQC and UTCHEM is that PHREEQC uses activities to describe reactions, whereas UTCHEM uses molalities (activity = activity coefficient \times molality; the activity coefficient is a function of, amongst other, the ionic strength of the solution). For comparison purposes, in this benchmark the activity coefficients in PHREEQC were set equal to 1 by modifying its database. Moreover, only reactions modelled in UTCHEM were activated in the PHREEQC database. The list of reactions is presented in Mohammadi *et al.* (2009). Furthermore, to allow for a comparison of the results, both simulators were run with the one-point upstream weighting option.

Table 1: Basic properties of the core and fluids of the benchmarking exercise.

Parameter	Value	Parameter	Value	Parameter	value
Length	61 cm (2 ft)	Water density	1010 kg/m ³	S_{orw}	0.25
Width	6.1 cm	Oil density	39.10 kg/m ³	S_{wc}	0.10
Height	6.1 cm	Water viscosity	1.0 cP	k_{rw}	1.0
Porosity	0.20	Oil viscosity	3.0 cP	k_{row}	1.0
Permeability	500 mD	Injection rate	0.005 ft ³ /d	n_w	2
				n_o	2

3.2.1. Oil displacement by water (Case WF)

This case is performed as a reference case to validate that both simulators produce identical results for oil-water displacement in the absence of chemical reactions. Figure 3 presents the results together with the analytical solution developed by Buckley and Leverett (1942). The initial water saturation in the core was set to 0.2. The agreement between the results of the two simulators is excellent. The discrepancy between the results of the simulators and the analytical solution is because of the numerical dispersion induced by the first-order numerical schemes of the simulators.

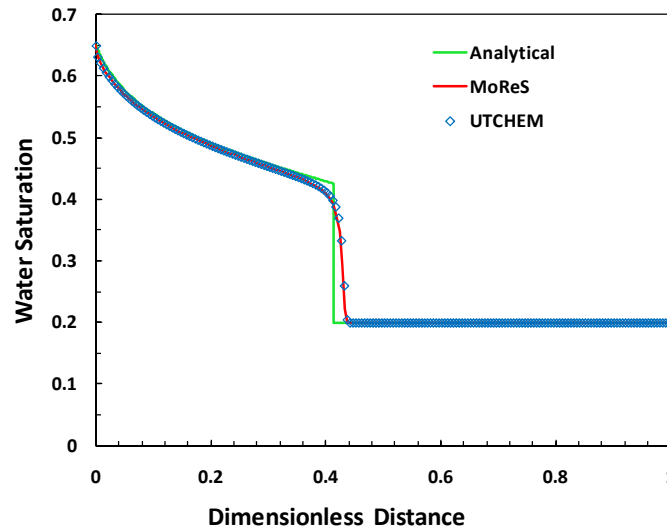


Figure 3: Oil displacement with water.

3.2.2. Alkaline injection with cation exchange (no oil, Case AF-Ex)

In this case a core initially saturated with brine of nearly neutral pH (7.5) is flooded with a solution with higher pH (11.1). The compositions of the initial and injected solutions are given in Table 2. The simulation considers the cation-exchange reactions, as explained in the previous section ($X=0.02$ mol/kg water). In Figure 4 we present graphs of the pH, Na^+ , CO_3^{2-} and HCO_3^- concentrations versus dimensionless distance (distance divided by the length of the core) for 0.15 and 0.4 PV injected. As can be seen from Figure 4 there is a good agreement between the results of the two simulators at the two different times. Without exchange reactions, and in the absence of physical dispersion, the transition from the high-pH region to the low-pH region is sharp and moves with the same speed as the injected water. However, when cation exchange is allowed in the simulation, at the front of displacement the alkaline is consumed (Eq. 7), as a result of which the concentration fronts lag behind the displacement front. For example after 0.40 PV of alkaline injection the front of carbonate (and other species) is at a dimensionless distance of 0.36 instead of 0.40. In this case, the hydrogen ions are detached from clay and are replaced by the sodium ions. This exchange process results in a dip in the pH graph and a reduction of sodium concentration in the Na plot. The extent of the delay and reduction in pH is directly dependent on the value of X . As a result of the reduction in pH, a small fraction of carbonate is converted to bicarbonate ions.

Table 2: Compositions of the initial and injected fluids of Case AF-Ex. The concentrations are expressed in mmol/kg water. The charge balance is obtained by modifying Cl⁻ concentration.

	Initial solution	Injected solution
pH	7.5	11.1
CO_3^{2-}	-	100
HCO_3^-	18	-
Na^+	40	220
Cl ⁻	32	22

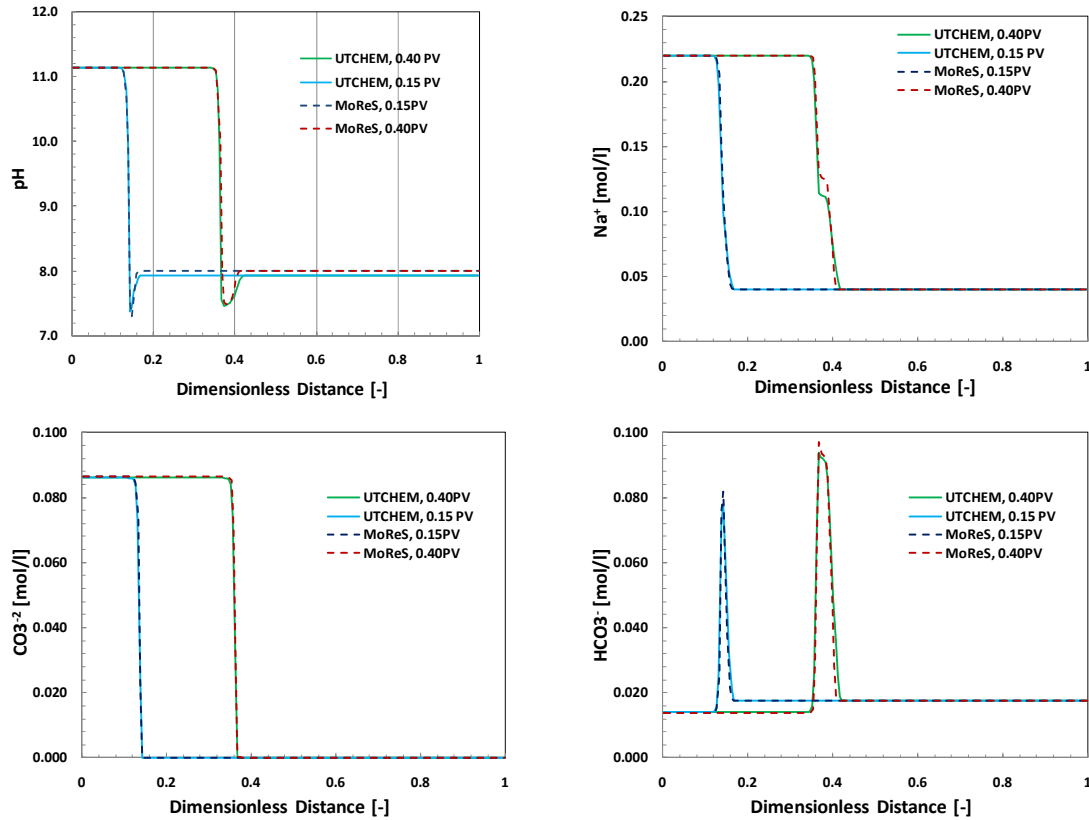


Figure 4: Alkali injection into a core initially saturated with brine with cation exchange reactions.

3.2.3. Alkaline injection with cation exchange in the presence of acidic oil (Case AF-Ex-TAN1)

In this section we compare the results of the case where an alkaline solution is injected into a core saturated with the oleic and aqueous phases, assuming a constant initial water saturation of $S_{wi} = 0.2$. The fluid properties of this case are presented in Table 3. The oleic phase contains naphthenic acids and its acid number is 1 mg KOH/g oil. We disregard the effect of soap on the IFT and consequently the generation of soap does not impact the displacement process of the oil by water. This means that we use the relative permeability parameters of Table 1. For numerical reasons, it was not possible to use the same residual oil saturation for water flooding (S_{orw}) and alkaline flooding (S_{orc}) in UTCHEM and therefore we set the residual oil to alkaline to 0.245 in UTCHEM. Moreover, similar to UTCHEM the charge balance was obtained by modifying pH of the solution. Figure 5 shows the concentration profiles of this case. Because oil is also present in the core, after 0.30 PV injection of alkaline, the fronts are at the dimensionless position of larger than 0.4. At the front of the displacement the acid is partitioned into the aqueous phase and eventually converted to soap. The values of k_{eq}^{HAw} and k_{eq}^P (Eqs. 2 and 3) are chosen to be the same in both simulators ($k_{eq}^{HAw} = 10^{-8}$ and $k_{eq}^P = 10^{-3.6}$). The small discrepancy between the results is because of the difference in the oil saturations. This is demonstrated in Figure 6, where we plot the profiles of oil saturation and acid concentration for both simulators. In UTCHEM alkaline injection produces slightly more oil compared to water flooding, which results in slightly delayed oil breakthrough compared to MoReS.

Table 3: Compositions of the initial and injected fluids of Case AF-Ex-TAN1. The concentrations are expressed in mmol/kg water. Charge balance obtained by modifying pH.

	Initial solution	Injected solution
pH	6.07	11.5
CO_3^{2-}	1	50
Na^+	325	525
Cl^-	325	325

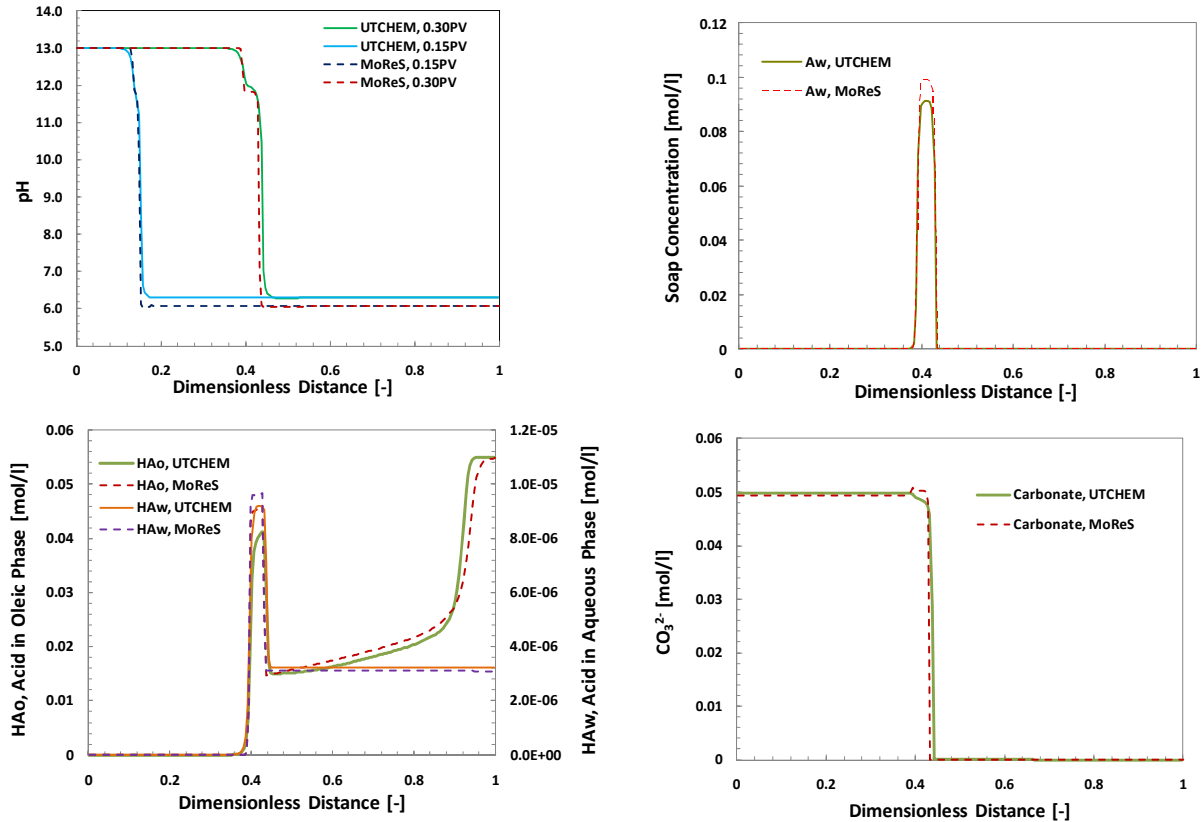


Figure 5: Alkali injection into a core initially saturated with brine and acidic oil with cation exchange reactions.

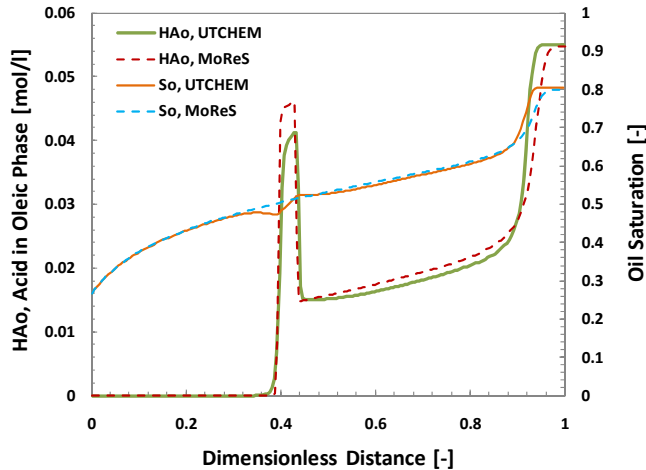


Figure 6: Profiles of oil saturation and acid along the core.

4. Description of the ASP model

The appearance of microemulsion (or middle phase as it forms between the oleic and aqueous phases) in the phase-behavior tests is usually interpreted as the sign of an active formulation that exhibits low IFT. This active formulation is usually selected for further evaluation in the coreflood experiments. Inclusion of microemulsion phase adds complexity to the models and requires data on the rheological and transport properties of the middle phase that are difficult to measure.

The alternative approach is to describe the lower surfactant-rich aqueous phase and the upper surfactant-rich oleic phase with a surfactant partition coefficient that is less than unity below optimum salinity and greater than unity above optimal salinity (Liu *et al.*, 2008). While it may be more correct to describe the Winsor III (optimum conditions) during the transition from Winsor I to Winsor II, the

transport of surfactant and low IFT can be modeled by the two phase model with less effort (Liu *et al.*, 2008, 2010).

4.1. Model assumptions

- Under all conditions, maximum of three phases (aqueous, oleic, and gas) can be present in the porous medium, meaning that the presence of the microemulsion phase is neglected. Fluid properties of the aqueous phase are updated each timestep based on the concentration of chemicals,
- The natural acids in the crude oil are collectively represented by a pseudo-acid $(HA)_O$ that upon reaction with alkali creates soap represented by A_w^- ,
- The kinetics of the reactions is not modelled. Therefore, all reactants instantaneously attain their equilibrium concentrations,
- The phase behavior of the soap/surfactant mixture is a function of the salinity. The soap and surfactant can partition into the aqueous phase with a salinity-dependent partitioning coefficient,
- IFT is a function of the salinity, concentrations of soap and surfactant, and the soap/surfactant ratio,
- Presence of the gas or polymer does not affect the phase behavior,
- The relative permeability parameters (end points, residual phase saturations, and Corey exponents) are functions of the capillary number and phase saturations. In other words, oil is mobilized only through lowering of IFT and increase of water viscosity,
- Pressure and volumes changes resulting from chemical reactions are not modeled. Moreover, we assume that chemical species in the phases do not occupy volume.
- The polymer transport properties are modeled similar to UTCHEM.

Further details of the model can be found in Mohammadi *et al.* (2009) and Liu *et al.* (2008).

4.2. IFT model and scaling of the fractional-flow parameters

A simplified version of Huh equation (Huh, 1979) is used to model the IFT. This equation relates the solubilization parameters, Z , to the IFT between the phases, σ (mN/m), by

$$\sigma = \frac{C}{Z^2} \quad (8)$$

C is an empirical constant and has been approximated to equal 0.3 from experimental data (Pope and Wade, 1992). It follows from this equation that an increase in the solubilization parameter (the volume ratio of the oil and water in the microemulsion phase) results in the reduction of IFT. Huh correlation has been originally developed to describe the IFT between the microemulsion phase and either of the oleic and aqueous phases. Nevertheless, we assume that it can also describe the IFT between the oleic and aqueous phases in the absence of the microemulsion phase in our model.

For the mixture of soap and surfactant the solubilization ratio, Z , depends on the optimum salinity of the mixture and the molar ratio of the soap and surfactant in the system. The details of the mixing rule for calculation of the solubilisation parameters for the mixture of soap and surfactant is described in Karpan *et al.* (2011). It has been shown experimentally that the oil recovery is higher with the combination of alkali and surfactant than with either injected alone (Reisberg and Doscher, 1956; Chiu, 1980). The additional oil recovery is because of the synergic effect of soap and surfactant (the IFT is lower for the mixture of the surfactant and the soap than for either taken alone) (Nelson *et al.*, 1984; Rudin and Wasan, 1992; Rudin *et al.* 1994). Therefore, the mixing rule, applied to model the IFT of the mixture, should be designed such that the IFT obtained by the mixture becomes lower than the IFT obtained by the soap or the surfactant alone. We neglect this effect in our current IFT model.

The relative-permeability parameters and residual phase saturations are scaled with the capillary number, using the equation employed in UTCHEM:

$$\xi(N_c) = \xi_c + \frac{\xi_w - \xi_c}{1 + T_c N_c} \quad (9)$$

where, ξ is any of the Corey model relative permeability parameters, for example S_{or} , ξ_w is the value at low capillary number (water flood conditions), ξ_c is the value at high capillary number (chemical flood conditions), and T_c is a scaling parameter. Transition from water-flood to chemical-flood relative permeabilities occurs around $N_c = 1/T_c$. The capillary number is calculated using Eq. (1) by inserting the values of the calculated IFT and the viscosity of the injected fluid for each grid block.

4.3. Optimum salinity

The optimum salinity of the mixture of soap and surfactant depends on the molar ratio of soap and surfactant in the solution (Liu *et al.*, 2008; 2010). A non-linear mixing rule proposed by Salager (1979) is used to calculate the optimum salinity of the mixture:

$$\ln P_{mix}^{opt} = X_{soap} \ln P_{soap}^{opt} + X_{surf} \ln P_{surf}^{opt} \quad (10)$$

In this equation P^{opt} is the optimum salinity, and X_{soap} and X_{surf} are the molar fractions of the soap and the surfactant in the mixture, respectively.

4.4. Partitioning of soap and surfactant

The acid, soap and surfactant are allowed to partition between the aqueous and oleic phases. The acid is partitioned between the phases with a constant partitioning coefficient according to Eq. (2). In the two phase model it is assumed that the transition from under-optimum to over-optimum conditions can be represented by a salinity-dependent partitioning coefficient for soap and surfactant. The partitioning coefficient is defined as:

$$K_i^P(P) = \frac{c_{io}}{c_{iw}} \quad , \quad (11)$$

where, c_{io} and c_{iw} are the molar concentrations of species i (i.e. soap or surfactant) in the oleic and aqueous phases. The basic assumption here is that at the optimal condition soap and surfactant are equally distributed between the phases, i.e. $K_i^P(P)=1$. Furthermore, when $K_i^P(P)>1$ the system is over-optimum and soap and surfactant are mostly in the oleic phase. When $K_i^P(P)<1$ the system is under-optimum and a large fraction of soap and surfactant partitions into the aqueous phase. Assuming that the partitioning coefficient is the same for both soap and surfactant, the following expression is used to evaluate its magnitude (Liu *et al.*, 2008):

$$\log_{10} K^P = \begin{cases} 2 \left(\frac{P}{P_{mix}^{opt}} - 1 \right) & \text{for } P > P_{mix}^{opt} \\ 2 \left(1 - \frac{P}{P_{mix}^{opt}} \right) & \text{for } P < P_{mix}^{opt} \end{cases} \quad (12)$$

where, K^P is the partitioning coefficient that is used for both soap and surfactant.

4.5. Calculation procedure

Figure 6 presents the schematic of the sequence of the operations in the current model. This figure is the detailed description of the boxes in Figure 1. Soap concentration and salinity are obtained from PHREEQC calculations. The values of X_{soap} and X_{surf} can be calculated using the amount of surfactant obtained from MoReS. The molar fractions of the soap and surfactant and the user-specified values of P_{soap}^{opt} and P_{surf}^{opt} are then inserted in Eq. (10) to update the value of the optimum salinity. Afterwards, the soap and surfactant are partitioned between the phases according to Eq. (12), where P is the value of the salinity obtained from PHREEQC. Langmuir type adsorption is assumed for adsorption of surfactant on the rock. The fluid-borne amounts of soap and surfactant are then used to calculate the soap/surfactant ratio, which together with user-specified solubilization parameters, salinity from

PHREEQC and calculated optimum salinity provides the IFT between the aqueous and oleic phase using Eq. (8). The polymer transport properties are modeled with a similar model to UTCHEM (see Karpan *et al.*, 2011). Viscosity of the aqueous phase is updated through the polymer model and is used to compute the capillary number by Eq. (1) and scale the relative permeability parameters using Eq. (9). The scaled parameters are then used in MoReS to solve the flow and transport equations and update the required parameters for the next timestep.

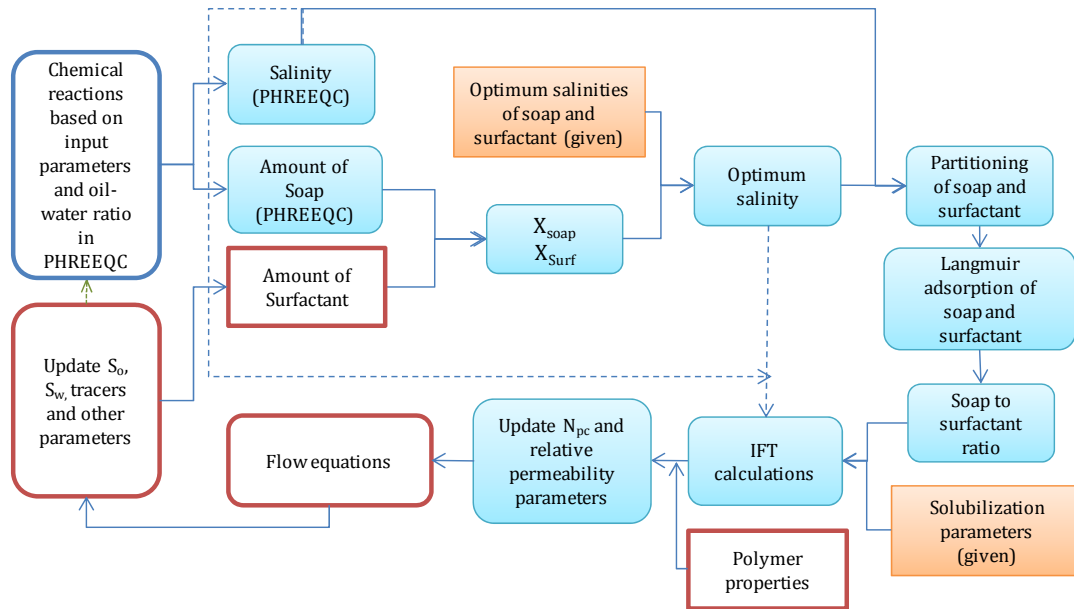


Figure 6: Schematic of the solution procedure.

5. History matching of an ASP experiment

In this section history matching of an ASP coreflood experiment with the current model is presented. In this experiment 0.30 pore volume (PV) of an ASP solution is injected into a water-flooded vertical core. The ASP solution was followed by injecting 2.4 PV of a polymer solution. The rock and fluid properties of the experiment are given in Table 4. The oil contains acid and its total acid number is 0.77 mg KOH/g oil. The composition of the initial and the injected fluids are presented in Table 5. The polymer concentration in the ASP and the drive polymer slugs were 3300 ppm and 2700 ppm, respectively. The surfactant concentration in the ASP slug was 3000 ppm.

Figure 7 illustrates the experimental oil production and pressure drop data (symbols) and compares them to the simulation results. The recovery factor is calculated based on the amount of the water-flood remaining oil. The simulated values agree well with the experiments. The oil breakthrough occurs at about 0.50 PV. At about 0.90 PV the oil in the experiment is produced in the form of an emulsion, and since we do not consider microemulsions in our model, the agreement is not perfect after production of the oil bank. The mismatch between the simulated and measured values in the pressure plot (after 0.90 PV) may be due to the retention of the polymer inside the core. The retained polymer can plug the core, decrease its permeability and result in higher pressure drops. For more details see Karpan *et al.* (2011) and Stoll *et al.* (2010).

The comparison between the measured and simulated pH, carbonate and bicarbonate profiles are presented in Figure 8. In general, the ASP model is capable of matching the concentration of the produced chemicals with a satisfactory accuracy. In Figure 9 we plot the soap, surfactant, salinity, and optimum salinity profiles along the core at the dimensionless time of 0.65 PV. As expected the injection of alkaline produces soap and reduces the optimum salinity of the system. The surfactant is moving behind the soap because of adsorption on the rock. At the front and behind the oil bank because of presence of both soap and surfactant the salinity is close to the optimum salinity. In the absence of the soap, the optimum salinity is that of the surfactant (16500ppm) and when the surfactant is not present the optimum salinity is that of the soap (5000 ppm).

Table 4: Basic properties of the core and fluids of the ASP experiment.

Parameter	Value	Parameter	Value	Parameter	value	Parameter	value
Length	30 cm	Water density	1015 kg/m ³	S_{orw}	0.30	S_{orc}	0.0
Diameter	5 cm	Oil density	900 kg/m ³	S_{wc}	0.09	S_{wcc}	0.0
Porosity	0.22	Water viscosity	0.6 cP	k_{rw}	0.115	k_{rwc}	1.0
Permeability	1800 mD	Oil viscosity	105 cP	k_{row}	1.0	k_{roc}	1.0
		Darcy velocity	1.0 ft/d	n_w	2.7	n_{wc}	1.2
		S_{wi}	0.09	n_o	1.8	n_{oc}	1.4

Table 5: Compositions of the initial and injected fluids of the ASP experiments. The concentrations are expressed in mmol/kg water.

	Initial solution	Injected solution
pH	7	11
HCO ₃ ⁻	12	-
CO ₃ ²⁻	-	95
Na ⁺	73	263
Cl ⁻	74	89
Ca ²⁺	0.55	-
Mg ²⁺	0.40	-

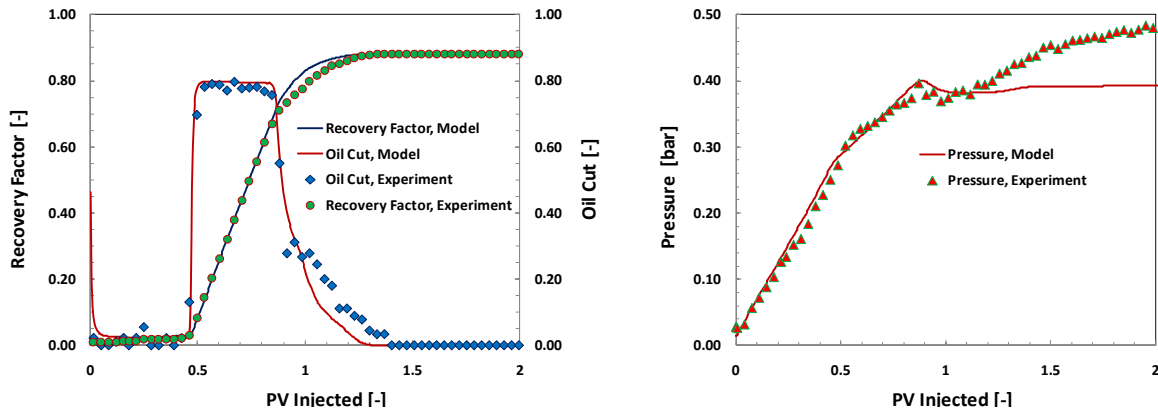


Figure 7: Comparison of the results of the ASP model with experimental data: oil recovery (left) and pressure data (right).

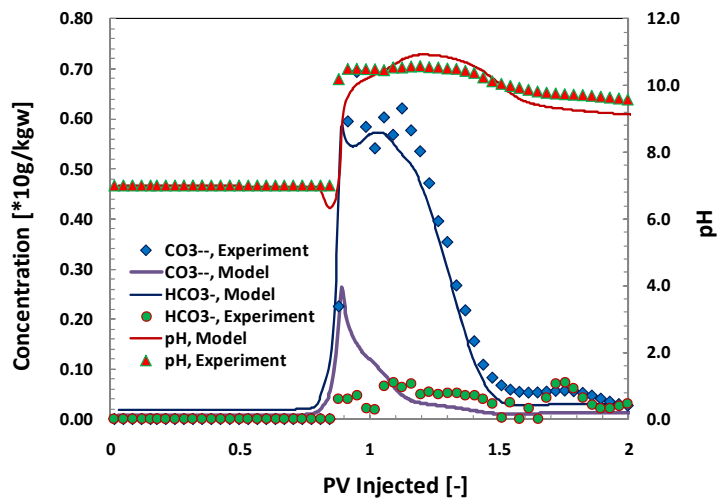


Figure 8: Comparison of the results of the ASP model with experimental data: pH, carbonate and bicarbonate ions.

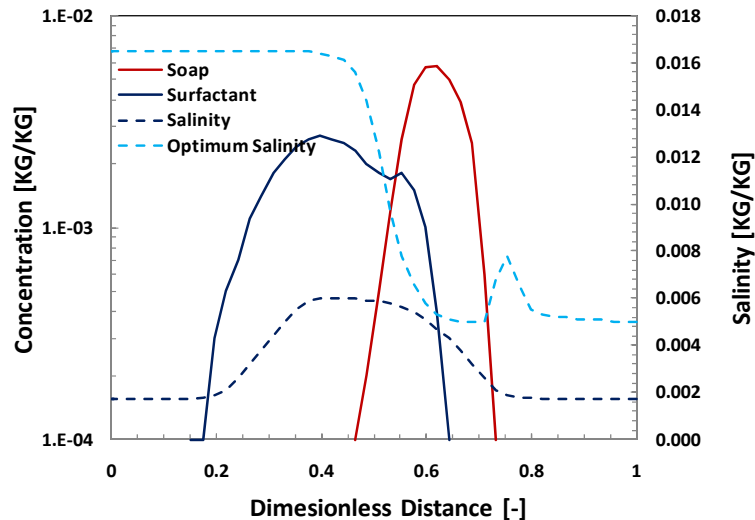


Figure 9: Profiles of simulated surfactant and soap concentrations, salinity and optimum salinity calculated from Eq. 10 at the dimensionless time of 0.65 PV.

6. Conclusions

- A multi-purpose dynamic reservoir simulator (MoReS) coupled to a geochemistry software program (PHREEQC) can account for the geochemistry involved with the Alkaline Surfactant Polymer floods,
- The saponification reaction was implemented by extending the database of PHREEQC with acid partitioning and acid dissociation,
- The results obtained from the PHREEQC-based saponification agrees well with the published experimental data for saponification reaction,
- The results of the propagation of the chemical species in porous media were benchmarked against UTCHEM and good agreement was obtained,
- An ASP coreflood experiment was modeled successfully taking into account the saponification reaction, cation exchange between the rock and the fluids and other possible reactions described in the database of PHREEQC,
- The coupling of MoReS to PHREEQC provides a versatile tool for simulating the chemically enhanced oil recovery processes.

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