

Modeling of Wettability Alteration during Spontaneous Imbibition of Mutually Soluble Solvents in Mixed-Wet Fractured Reservoirs

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Abstract—Mutually-soluble solvents can enhance oil recovery both in mixed-wet fractured reservoirs. When a partially water-wet matrix is surrounded by an immiscible wetting phase in the fracture, spontaneous imbibition is the most important production mechanism. Initially, the solvent moves with the imbibing brine into the core. However, upon contact with oil, as the chemical potential of the mutual solvent is different in both phases, diffusion occurs and the solvent is transported in the oleic phase. Through the migration of the mutually soluble component from the aqueous phase into the oleic phase, oil properties and/or rock-fluid interactions are modified. The hypothesis in this work is that a mutually-soluble solvent improves the ultimate recovery and the imbibition rate in mixed-wet cores. The main recovery mechanisms are the wettability change of the mixed-wet cores, oil swelling and oil viscosity reduction.

In this paper the numerical modeling of spontaneous imbibition of Mutually soluble solvent in mixed-wet cores is presented. We implemented the wettability alteration, the oil swelling mechanism, the oil viscosity reduction mechanism, the IFT reduction, and the density reduction mechanisms in the numerical model. Our numerical studies show that the most important production mechanism in the mixed-wet systems are the oil swelling and the wettability alteration and the second most important mechanism is the oil viscosity reduction. The effect of the IFT reduction and the density reduction in the oil production is not significant. The numerical results show an improvement of 27%.

Keywords: Enhanced oil recovery, Mutually soluble solvent, Numerical modeling, COMSOL, Fractured reservoirs, Spontaneous imbibition, wettability alteration.

I. INTRODUCTION

Naturally fractured reservoirs contain about 20% of the world's oil reserves and production [20]. From the engineering point of view, reservoirs with naturally occurring fractures that affect the fluid flow significantly, are considered fractured reservoirs[21]. Production from fractured reservoirs depends on matrix-fracture interaction [25]. In reservoirs with low permeable matrix blocks; oil wet matrix blocks and highly viscous oils, the transfer rate between fractures and matrix is slow and consequently the recovery is low. When a strongly or partially water-wet matrix is surrounded by an immiscible wetting phase in the fracture, spontaneous imbibition is the most important production mechanism [18]. Since the spontaneous imbibition process is largely dominated by capillary diffusion, the parameters that control the capillary forces will affect the spontaneous imbibition process, i.e., the wetting properties of the matrix - fluid [4], [22], two phase flow properties, e.g., rel-perm and capillary pressure functions[2], [3], [1],

the matrix permeability[17], viscosities of the phases[16], the initial water saturation[14], and the boundary conditions [12]. Mutually-soluble solvents (MSS) [23] can accelerate and enhance the matrix-fracture transfer rate[5]. Due to the migration of the mutually soluble component from the aqueous phase into the oleic phase, both the oil properties and/or rock-oil interactions are modified. For instance the oil mobility (permeability/viscosity) [19] may increase and this may enhance the ultimate recovery and the imbibition rate in the fractured reservoirs [9]. An additional contributor to enhanced recovery is oil swelling; when solvent diffuses in the oil phase, the volume of the oil in the porous medium increases. The oil swelling improves oil recovery in two ways: first, when oil ganglia swell, they occupy more pore space. Consequently, the oil saturation increases leading to a higher oil relative permeability [11]. Secondly, after introducing the solvent in the core the residual oil is not pure oil but it contains solvent, and for a given residual oil saturation less pure oil stays behind. Other mechanisms that affect recovery are oil density reduction [23] and an alteration of the oil-water interfacial tension [7], [8]. However, the solvent will not reduce IFT sufficiently for a significant increase in recovery as shown in the capillary de-saturation curve [13]. However, imbibition rate and total recovery could be improved with the wettability alteration of the rock to the more favorable water-wet condition[24], [6], [15], [10]. We developed a model that describes solvent/brine imbibition into a petroleum filled core. We use rel-perms and capillary pressure that is characteristic of water-wet and mixed-wet cores. Model equations are solved with a commercial finite element package (COMSOL). Interfacial tensions were obtained from separate laboratory experiments. We optimized correspondence between experiment and theory by modifying the sorting factor and end points. Oil viscosities were obtained from an empirical relation (fourth power law); the ideal mixing law (partial molar volumes independent of composition) was used as an equation of state (EOS). Solubility characteristics were taken from the literature. For the diffusion coefficient in the liquid we used the Wilke-Chang relation. Good agreement between experiment and theory was obtained.

A. Experimental study

The experimental procedure has been discussed in the paper [4]. A core was saturated first, then it was brought in an Amott imbibition cell (see Figure 1), which was subsequently filled with brine with or without solvent, to perform spontaneous imbibition experiments. The core sample was placed

vertically on a small glass cross at the bottom of the lower part of the Amott cell. The upper and the lower part of the Amott cell were attached together with clamps. Brine solution was poured gradually into the Amott cell and the core was exposed to MSS/brine. After that production effectively stops, the core was moved to another Amott imbibition cell, which was subsequently filled with a mixture of MSS/brine.

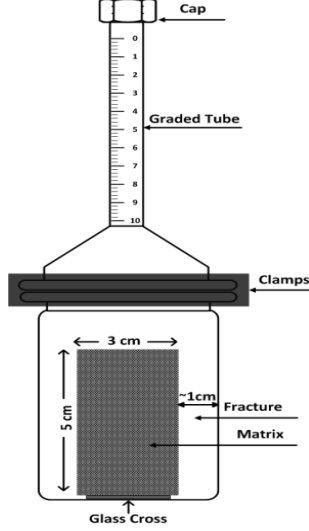


Fig. 1: Schematic drawing of an Amott imbibition cell. An oil filled core is placed at the middle of the lower part. The upper part is attached to the lower part with clamps. The Amott cell is gradually filled with an aqueous phase from the top until it reaches to the zero level in the graded cylinder; then the cap is closed.

II. NUMERICAL MODELING

The purpose of this work is to understand the physics of the spontaneous imbibition of the MSS into a single matrix which is surrounded by fractures. Our experimental observation is that the imbibition of an aqueous phase is enhanced by adding a MSS. In order to study the governing mechanisms of the oil recovery by spontaneous imbibition, a numerical model was developed and the numerical model equations were solved using a commercial finite element package (COMSOL Multiphysics). In the following section, we will describe the numerical modeling of some selected experiments.

A. Model description

The imbibition occurs in a cylindrically symmetric geometry (core). The vertical cross-section of the cylinder is a rectangular plane. We developed a 2D axisally-symmetric, 2-phase and 3-component model for the MSS-aided spontaneous imbibition in a matrix block that is surrounded by fractures. The initial condition and boundary conditions were established assuming capillary-gravity equilibrium. First, we optimized the correspondence between experimental primary recovery (recovery with brine) and the simulation by modifying the sorting factor and relative permeability end points. Afterwards, the proper relative permeability and capillary pressure functions

were used to model the spontaneous imbibition of the solvent/brine mixture into the core. The mass conservation law for the oil, brine and solvent components were supplemented with Darcy's law. Therefore, the model equations for spontaneous imbibition of the solvent/brine mixture into an oil filled core are

$$\sum_{\alpha=1}^N \left(\frac{\partial}{\partial t} (S_{\alpha} V_{\alpha c}) + \nabla \cdot (V_{\alpha c} u_{\alpha} (S_{\alpha}, V_{aw}, P_{\alpha})) - \nabla \cdot (\varphi D_{sc} S_{\alpha} \nabla \cdot V_{\alpha c}) \right) = 0, \quad \alpha = o, a; \quad c = h, w, s, \quad (1)$$

where S_{α} denotes the saturation of the phase α , P is the pressure of the phase α , $V_{\alpha c}$ is the volume fraction of the solvent in phase α , i.e., V_{aw} is the volume fraction of the water component in the aqueous phase, u_{α} is the Darcy velocity of the phase α , which is calculated from Darcy's equation (equation 2), D_{sc} is the molecular diffusion of the solute (MSS) in the aqueous or in the oleic phase. The subscripts a, o, s, w and h denote the aqueous phase, the oleic phase, the solvent component, the water component and the hydrocarbon component, respectively. A similar set of equations was used to simulate the spontaneous imbibition of brine into the core. The Darcy velocity for the phase α is defined by

$$u_{\alpha} (P_{\alpha}, V_{aw}, S_{\alpha}) = - \frac{K k_{r\alpha} (S_{\alpha})}{\mu_{\alpha} (V_{aw})} \nabla \cdot (P_{\alpha} + \rho_{\alpha} (V_{aw}) g z), \quad (2)$$

where K is permeability, $k_{r\alpha}$ is relative permeability of the phase α , μ_{α} is the viscosity of phase α , ρ_{α} the phase density, g is gravitational acceleration, and z is the upward vertical distance from the bottom of the core.

The molecular diffusion of the solute (MSS) in the oleic phase or in the aqueous phase is calculated from the Wilke-Chang correlation [26]

$$D_{sc} = 7.4 \times 10^{-8} \left(\frac{T (\phi_c M_c)^{1/2}}{\mu_c \hat{V}_s^{0.6}} \right),$$

where ϕ_c is the association parameter of the solvent $c = h, w$, M_c is the molecular weight of the solvent c , μ_c is dynamic viscosity of the solvent c in centipoise, \hat{V}_s is molar volume of the MSS (= the volume of a mole of pure solute (MSS) at its normal boiling point) in cm^3/mol and T is temperature in Kelvin. The system of equations is not closed. Since there are 8 unknowns with 3 equations, we need five additional auxiliary equations to complete the model, viz.

$$\sum V_{ac} = 1, \quad c = w, s, \quad (3)$$

$$\sum V_{oc} = 1, \quad c = h, s, \quad (4)$$

$$\sum S_{\alpha} = 1, \quad \alpha = o, a, \quad (5)$$

$$P_c (S_{\alpha}) = P_a - P_o, \quad (6)$$

where P_c is capillary pressure function, V_{oh} is the volume fraction of the hydrocarbon in the oleic phase. The capillary pressure function is described using the Brooks-Corey correlation

$$P_c (S_{\alpha}) = P_{ct} S_e (S_{\alpha})^{(-1/\lambda)}, \quad (7)$$

where P_{ct} is the threshold capillary pressure which corresponds to required entry pressure for the aqueous phase to flow into the core and it is defined as

$$P_{ct} = \gamma \sigma \sqrt{\frac{\varphi}{K}} \left(\frac{0.5 - S_{wc}}{1 - S_{wc} - S_{or}} \right)^{(1/\lambda)} \quad (8)$$

where γ is a fitting parameter for the capillary pressure curve, σ is the interfacial tension, φ is porosity of the rock, K is the permeability of the rock, S_{wc} is connate water saturation, S_{or} is residual oil saturation, λ is sorting factor and S_a is the saturation of the aqueous phase. The capillary pressure curve is extended below the connate water saturation to avoid infinite capillary pressures in this range of saturation. Moreover, S_e is the effective saturation of the aqueous phase and it is defined as

$$S_e(S_a) = \frac{S_a - S_{wc}}{1 - S_{wc} - S_{or}}, \quad (9)$$

The relative permeabilities use the residual oil saturation and the sorting factor as fitting parameters. The relative permeability curves were also estimated from Brooks-Corey correlation

$$k_{ra}(S_a) = k_{ra}^e S_e(S_a)^{(3+2/\lambda)}, \quad (10)$$

$$k_{ro}(S_a) = k_{ro}^e (1 - S_e(S_a))^2 (1 - S_e(S_a))^{(1+2/\lambda)}, \quad (11)$$

where k_{ra}^e is the end-point for the aqueous phase relative permeability curve and k_{ro}^e is the end-point for the oleic phase relative permeability curve.

1) *oil swelling mechanism*: The mechanism of the oil swelling is satisfied with the compositional formulation which is already implemented as the model. Both the oleic and the aqueous phase are incompressible so the system of equation was presented in volumetric forms. In this system all physical properties of the oleic phase and the aqueous phase like density and viscosity are presented as a function of volume fraction of the components in the phases.

2) *Modeling of the wettability alteration*: A contributor mechanism to the oil recovery by the MSS/brine spontaneous imbibition is wettability modification. In this section we will describe the procedure of the implementation of this mechanism in the numerical model. For the time being, a time dependant ramp function was defined to correlate the relative permeability functions and capillary pressure function at the beginning of the MSS/brine imbibition and at the end of the process (see Figure 2). End points, the sorting factor, the contact angle and the interfacial tension are clearly modified through the MSS/brine imbibition. Therefore, the involvement of the parameters that are infected by the MSS is decreased from an initial value at the beginning of the experiment, when it is just surrounded by MSS/brine to a final value through a constant rate with time.

$$P_c(S_a(t)) = (1 - \omega(t)) P_c^i(S_a(t)) + \omega(t) P_c^f(S_a(t)), \quad (12)$$

$$k_r(S_a(t)) = (1 - \omega(t)) k_r^i(S_a(t)) + \omega(t) k_r^f(S_a(t)), \quad (13)$$

where P_c^i and k_r^i are initial capillary pressure and initial relative permeability curves, which were obtained from matching of the brine imbibition. P_c^f and k_r^f are final capillary pressure curve and final relative permeability curve at the end of the solvent/brine imbibition. $\omega(t)$ is a time dependant ramp function, $\omega(t)$ is defined as

$$\omega(t) = \begin{cases} 0 & \text{if } t = 0 \\ 1 & \text{if } t = \frac{1}{\beta} \\ \frac{1}{\beta} \times t & \text{if } 0 < t < \frac{1}{\beta} \end{cases} \quad (14)$$

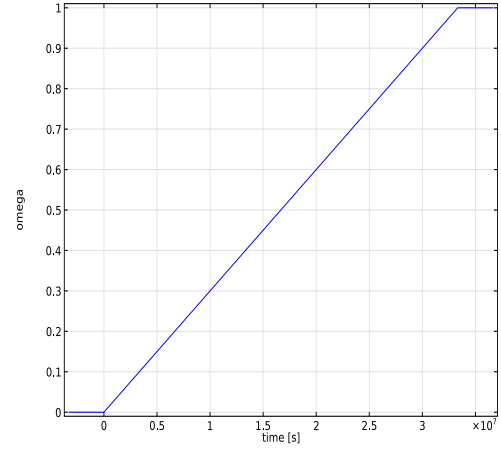


Fig. 2: A typical time ramp function; the solvent improves the wettability of the core to a more water-wet condition. The modification occurs during the imbibition of the solvent/brine into the core. The ramp function is time dependant, which is implemented to correlate the rel-perm curve and the capillary pressure curve at the beginning and the end of the process.

which β is the slope of the ramp function and it is obviously a fitting parameter. Figure 2 depicts a typical ramp function for a wettability modification process.

3) *viscosity reduction*: Another mechanism that is contributing in the oil recovery is viscosity reduction. This mechanism is implemented in the model in the form of the equations (15-16), where the viscosity of the oleic phase and the viscosity of the aqueous phase are obtained from quarter-power law

$$\mu_a(V_{aw}) = \left(\frac{V_{aw}}{\mu_W^{-1/4}} + \frac{V_{as}}{\mu_S^{-1/4}} \right)^{-4}, \quad (15)$$

$$\mu_o(V_{aw}) = \left(\frac{V_{oh}}{\mu_H^{-1/4}} + \frac{V_{os}}{\mu_S^{-1/4}} \right)^{-4}, \quad (16)$$

where V_{as} is the volume fraction of the solvent in the aqueous phase, V_{os} is the volume fraction of the solvent in the oleic phase, μ_W is the viscosity of pure brine and μ_H is the viscosity of pure hydrocarbon and μ_S is the viscosity of pure solvent. The viscosity of the oleic phase in terms of oil concentration is described in Figure 3

4) *Oil density reduction*: The density reduction mechanism is fulfilled through the volume weighted mixing law, that means the density of the phases are determined using the volume concentration of the phase from below equation. Figure 4 shows the density of the oleic phase as a function of the oil concentration.

$$\rho_a(V_{aw}) = \frac{1}{\frac{V_{as}}{\rho_S} + \frac{V_{aw}}{\rho_W}} \quad (17)$$

$$\rho_o(V_{aw}) = \frac{1}{\frac{V_{os}}{\rho_S} + \frac{V_{oh}}{\rho_H}} \quad (18)$$

5) *Interfacial tension reduction mechanism*: MSS reduces the oil water interfacial tension. This mechanism contribute in

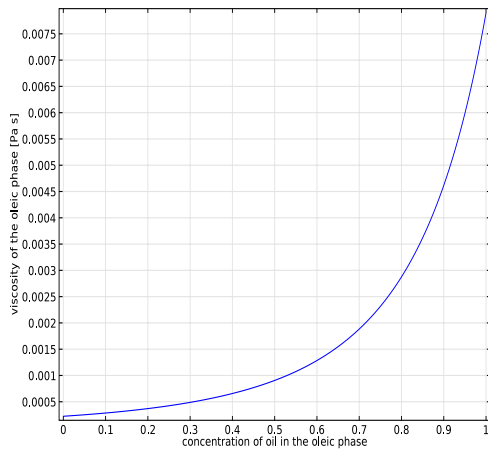


Fig. 3: The viscosity of the oleic phase is determined from the quarter power law.

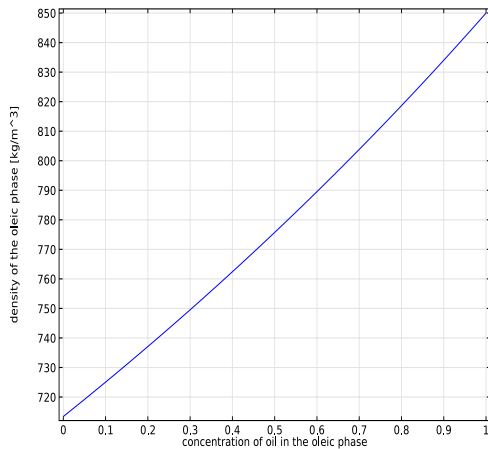


Fig. 4: The density of the oleic phase is determined from the volume weighted mixing law.

the oil recovery very slightly. In order to take the effect of the IFT reduction in the oil recovery, a time ramp function with a different slope than the slope for the wettability alteration was applied.

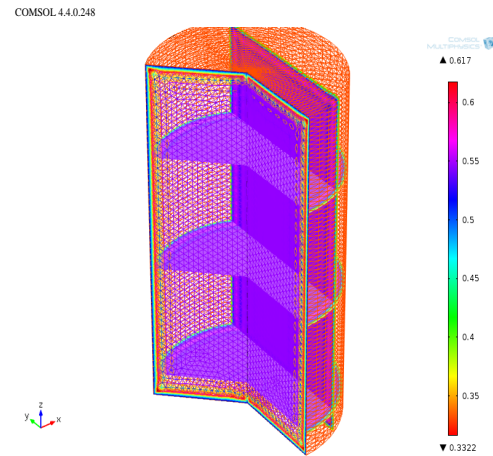


Fig. 5: Distribution of the hydrocarbon in the core is shown. The distribution of the oil concentration is obtained from the solution of the numerical model at time 2.4×10^6 seconds. The wireframe and the distribution of the oil concentration in the cut planes in the yz plane and xy planes are shown in the picture.

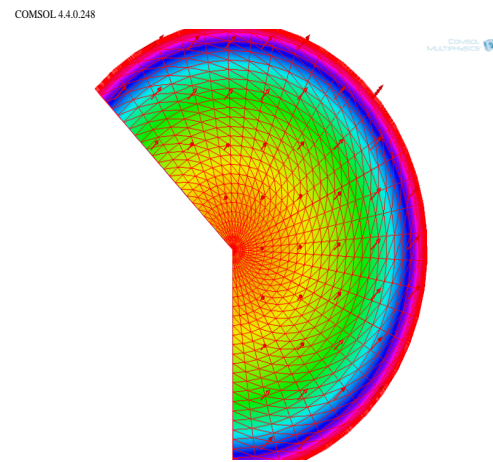


Fig. 6: Distribution of the water concentration in the aqueous phase in the core is shown. The distribution is obtained from the solution of the numerical model at time 4.55×10^6 seconds. Arrows show upstream hydrocarbon concentration toward downstream hydrocarbon concentration.

6) *Partitioning of the solvent*: The governing mechanisms in the spontaneous imbibition of MSS are strongly influenced by the distribution of the solvent into the oil phase. The distribution of the solvent in the oil phase is quantified by partition coefficient, that is defined as the volume fraction of the solvent in the oleic phase divided by the volume fraction of the solvent in the aqueous phase

$$V_{as} = HV_{oh}, \quad (19)$$

where H is partition coefficient of the solvent.

7) *Initial and boundary conditions*: The initial and boundary conditions were defined by the application of the capillary-gravity equilibrium around the core. The integrated oil produc-

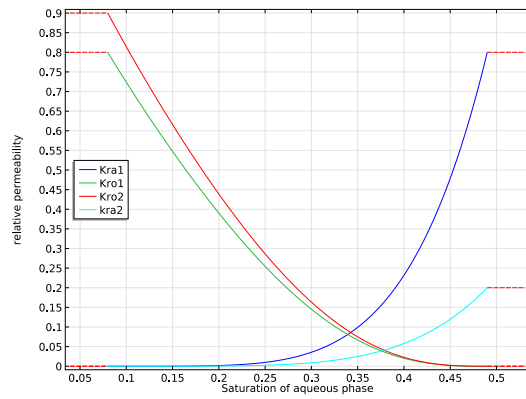


Fig. 7: In order to apply the effect of wettability alteration in the simulation two sets of rel-perm curves were used at the beginning and the end of the spontaneous imbibition process. The relative permeability curves at the beginning (K_{ra1} and K_{ro1}) and the end (K_{ra2} and K_{ro2}) of the process are shown in the picture. Both the end points and curvature of the functions have been changed.

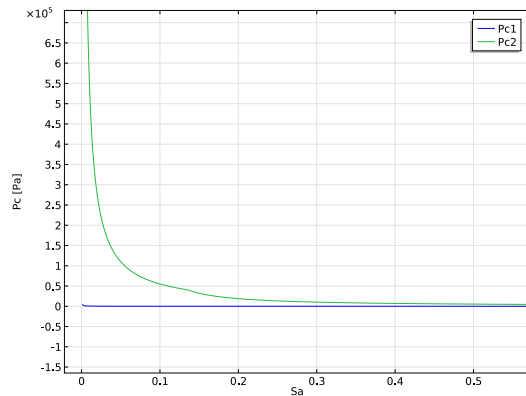


Fig. 8: In order to apply the effect of wettability alteration in the simulation two sets of rel-perm curves were used at the beginning and the end of the spontaneous imbibition process. The relative permeability curves at the beginning (K_{ra1} and K_{ro1}) and the end (K_{ra2} and K_{ro2}) of the process are shown in the picture. Both the end points and curvature of the functions have been changed.

tion through the whole domain was used to calculate the oil recovery curve.

8) *Weak formulation:* Then the model equations were converted to weak form and they were implemented in a commercial equation based finite element package (COMSOL Multiphysics). The relative correspondence between results and numerical model was modified using the fitting parameters, e.g., sorting factor, end-points, slope of the ramp function, residual oil saturation, etc. Figure 5 shows the slices of the concentration of water cut plane distribution of the hydrocarbon in the core, which is obtained from the numerical model at time 4.55×10^6 seconds. Arrows show upstream hydrocarbon concentration toward downstream hydrocarbon concentration.

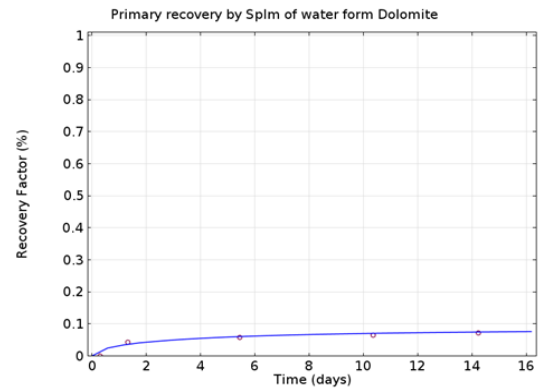


Fig. 9: A good agreement between the numerical model and the spontaneous imbibition on the MWD1 core. Numerical modeling of the primary oil recovery by spontaneous imbibition of brine into an oil-filled mixed-wet Dolomite core (MWD1). Our model shows that brine imbibes to the core due to capillary diffusion. The primary recovery of 7% of OOIP was predicted by the numerical model.

III. CASE STUDY

The prediction of the oil recovery by brine imbibition from MWD1 core is shown in Figure 9. The porosity and the permeability of the core are 18.8% and 171 mD respectively. The driving force for the penetration of brine into the core is capillary diffusion. However, the oil recovery is very low, i.e., 7% of the OOIP. The difference between the relative permeability curves and the capillary pressure curves at the beginning and the end of the modeling are presented in Figure 7 and Figure 8. Moreover, the numerical model predicts an extra oil recovery of 27% of the OOIP, which is in good agreement with the the oil recovery from the experiment of solvent/brine imbibition. The simulated model and the experimental data are presented in Figure 10. Here, the main contributing mechanisms to the oil recovery are the wettability alteration and the oil swelling; the viscosity reduction is another contributing mechanism. But, interfacial tension reduction does not play an important role in the oil recovery.

Relative permeability functions of core MWD1 is presented in Figure 7. The model predicts that the ramp slope β for this study is $3 \times 10^{-8} s$.

IV. CONCLUSIONS

- The presence of a MSS solvent can enhance the spontaneous imbibition oil recovery. For mixed-wet dolomite the primary and secondary recovery is 7% and 27% respectively.
- A numerical model is developed that describes the wettability alteration during the solvent enhanced imbibition process.

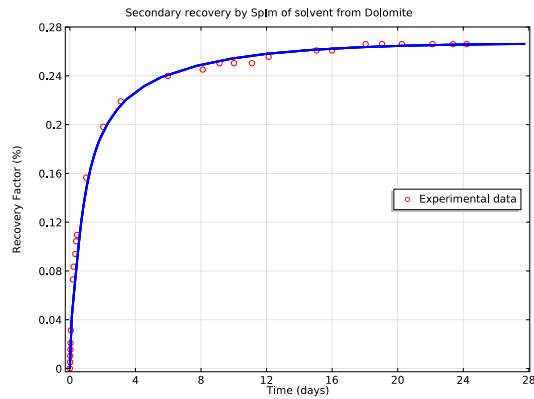


Fig. 10: The numerical modeling of the primary oil recovery by spontaneous imbibition of brine into an oil-filled mixed-wet Dolomite core (MWD1). The slope of the time ramp for the wettability alteration mechanism (β) is $3 \times 10^{-8} s$. There is a deviation in plot which probably correspond to the attaching of drops to the rock surface.

V. NOMENCLATURE

S_a ,	Saturation of aqueous phase
S_o ,	Saturation of oleic phase
u_o ,	aqueous phase Darcy velocity
u_a ,	oleic phase Darcy velocity
P_a ,	Pressure of the aqueous phase, Pa
P_c ,	Capillary pressure, Pa
V_{aw} ,	Volume fraction of water in the aqueous phase
V_{oh} ,	Volume fraction of water in the oleic phase
V_{as} ,	Volume fraction of solvent in the aqueous phase
V_{os} ,	Volume fraction of solvent in the oleic phase
D_{sa} ,	Molecular diffusion of solvent in the aqueous phase
D_{so} ,	Molecular diffusion of solvent in the oleic phase
K ,	Rock permeability, m^2
k_{ro} ,	Oleic phase relative permeabilities
k_{ra} ,	Aqueous phase relative permeabilities
k_{ro}^e ,	Oleic phase end-point relative permeabilities
k_{ra}^e ,	Aqueous phase end-point relative permeabilities
t ,	Time, s
T ,	Temperature, K
M ,	Molecular weight, s
\hat{V}_s ,	Molar volume of s, cm^3/mol
ϕ ,	Parameter of association
φ ,	Porosity
λ ,	Sorting factor
α ,	Oleic or aqueous phase
β ,	the slope of the ramp function
ρ_α ,	Density of the phase α , kg/m^3
g ,	Gravitational acceleration m^2/s
S_{wc} ,	Connate water saturation
S_{or} ,	Residual oil saturation
μ_α ,	Viscosity of phase α , Pa·s
σ ,	Aqueous oleic interfacial tension, N/m
γ ,	Capillary pressure tuning parameter
o ,	oleic phase
a ,	aqueous phase
s ,	solvent component
w ,	water component
h ,	hydrocarbon component
$OIIP$,	Original Oil In-Place
MWD ,	Mixed-wet Dolomite

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