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PREFLOOD DESIGN FOR CHEMICAL FLOODING-- A STUDY ON ION EXCHANGE/DISPERSION PROCESS IN POROUS MEDIA

by

C. S. Chiou

and

H. L. Chang

Abstract:

Ionic composition of surfactant systems is an important determinant of chemical-flood oil-recovery processes. In order to provide a favorable environment for the surfactant fluid, reservoir preconditions may be required. One technique is to inject a preflood of specific salinity water that will replace the formation brine and condition the clays by ion exchange. However, it has been shown that an improperly designed preflood can impair, rather than improve, the effectiveness of the surface-active agents. It is the purpose of this work to study theoretically and experimentally the combination effect of ion exchange (between the preflood fluids and reservoir clays) and dispersion (in the porous media) on the preflood performance.

A mathematical model for the ion exchange/dispersion process in linear porous media has been developed for the three components system (Na^+, Ca^{++} and Mg^{++}). The results would give a better understanding for the kinetic aspect of ion exchange as well as to evaluate preflood performance for chemical flooding.

I. Introduction

The presently available formulations for micellar slug are intolerant of high salinity. Generally, if the salinity is higher than a few percent, the oil displacement is unsatisfactory, and further, the presence of undesirable divalent cations (calcium and magnesium) in the micellar fluid have an adverse effect upon the ability of the surface-active agents. It is the intent of the preflood to replace the formation water to reduce the salinity and divalent cation concentration in the reservoir to an acceptable level before introducing the surfactant. However, oil recovery in field pilot tests shows that beneficial effect are not assured by preflooding, since an improperly designed preflood can impair, rather than improve, the effect of a slug. It is now acceptable that preflood types and reservoir clays play important roles in determining the ionic composition in the front of the surfactant slug under operative condition. It is the purpose of this work to study theoretically and experimentally the combination effect of ion exchange and dispersion on the preflood performance.

A mathematical model for a one dimensional miscible displacement process involving ion exchange has been developed. This model is based on assumed rates of cation transfer between flooding water and reservoir solids. A numerical technique was used to solve the nonlinear partial differential equations for the three components (Na^+, Ca^{++}, and Mg^{++}) system. The present mathematical model with the laboratory experiments would be able to give a better understanding of the kinetics aspect of ion exchange as well as to evaluate preflood performance in chemical waterflooding process. Furthermore, it is hoped that a set of design criteria can be put forward for the preflood to provide optimum ionic environment for the surfactant flooding.

II. Model Formulation

In the following, we discussed the formulation of ion exchange/ dispersion process in a three-component system consisting of sodium, calcium and magnesium ions. In this report the equilibrium among these ions between the flooding water and rock surfaces is assumed to follow a fairly broadly used emperical formulation, known as "mass-action" equation,

$$\frac{\overline{C}_{Na}}{\overline{C}_{Ca}^{\,1/2}} = K_1 \frac{C_{Na}}{C_{Ca}^{\,1/2}} \quad (1)$$

$$\frac{\overline{C}_{Ca}}{\overline{C}_{Mg}} = K_2 \frac{C_{Ca}}{C_{Mg}} \quad (2)$$

where C is the concentration of the indicated ion in solution and $\overline{C}$ is the concentration of the ion on clays in equilibrium with the solution, and K_1 and K_2 are the experimentally determined equilibrium constants. Here K_1 and K_2 are dimensionless and determined to be 0.15 and 2.0 respectively. We recognize that these K values are functions of the type of clay, the ionic composition of the flooding water, and temperature. In practical field application, variation of rock samples complicates the determination of representative K values.

Inspection of equation (1) shows that if the sodium ion is increased, some of the excess sodium ion will be adsorbed while some of the calcium ion will be desorbed in order to maintain the equilibrium value constant. The converse is also true. Furthermore, equation (2) shows that if K_2 approaches unity, there will be no selectivity between calcium and magnesium ions, or in other words, calcium and magnesium can be treated as a single divalent ions.

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Under nonequilibrium conditions, the instantaneous cation, $\overline{C}_i$, on the rock surface deviates from $\overline{C}_{i,\,eq}$, which is the cation concentration on rocks being in equilibrium with the interstitial solution of concentration C_i. The extent of this deviation depends on the ion exchange rate. The rate may be conveniently approximated by simple "linear-driving-force" relations[1]:

$$\frac{\partial \overline{C}_i}{\partial t} = K_R \left(\overline{C}_{i,\,eq} - \overline{C}_i\right) \qquad (3)$$

where K_R is the ion exchange rate constant. This relationship implies that at any time, the ion exchange rate is proportional to the concentration change between the instantaneous and the equilibrium states. Notice that the present rate equation assumes no concentration gradient in the liquid/ solid interface.

The one-dimensional transport equation for component i may be given as:

$$\phi \frac{\partial}{\partial t}\left(C_i + \overline{C}_i\right) - V \frac{\partial C_i}{\partial x} + D \frac{\partial^2 C_i}{\partial x^2} = 0 \qquad (4)$$

where

ϕ = Porosity

V = Superficial velocity of the fluid

D = Dispersion coefficient

x = Distance from the column entrance

t = Time

We assume the total exchangeable cation concentration on the rock surface is equal to the cation exchange capacity (Q_v, a constant), or

$$\overline{C}_{Na} + \overline{C}_{Ca} + \overline{C}_{Mg} = Q_v \qquad (5)$$

Combination of equations (1) through (5) gives the complete set of nine equations for the ion exchange/dispersion system:

$$\phi \frac{\partial}{\partial t}\left(\overline{C}_{Na} + C_{Na}\right) - V \frac{\partial C_{Na}}{\partial x} + D \frac{\partial^2 C_{Na}}{\partial x^2} = 0 \qquad (6)$$

$$\phi \frac{\partial}{\partial t}\left(\overline{C}_{Ca} + C_{Ca}\right) - V \frac{\partial C_{Ca}}{\partial x} + D \frac{\partial^2 C_{Ca}}{\partial x^2} = 0 \qquad (7)$$

$$\phi \frac{\partial}{\partial t}(\overline{C}_{Mg} + C_{Mg}) - V \frac{\partial C_{Mg}}{\partial x} + D \frac{\partial^2 C_{Mg}}{\partial x^2} = 0 \qquad (8)$$

$$\frac{\partial \overline{C}_{Na}}{\partial t} = K_R (\overline{C}_{Na,\, eq} - \overline{C}_{Na}) \qquad (9)$$

$$\frac{\partial \overline{C}_{Ca}}{\partial t} = K_R (\overline{C}_{Ca,\, eq} - \overline{C}_{Ca}) \qquad (10)$$

$$\frac{\partial \overline{C}_{Mg}}{\partial t} = K_R (\overline{C}_{Mg,\, eq} - \overline{C}_{Mg}) \qquad (11)$$

$$\overline{C}_{Ca,\, eq} = \frac{2\left(1 + \frac{C_{Mg}}{2C_{Ca}}\right) Q_v + \left(\frac{0.15\, C_{Na}}{C_{Ca}^{1/2}}\right)^2 - \sqrt{\left[2\left(1 + \frac{C_{Mg}}{2C_{Ca}}\right) Q_v + \left(\frac{0.15\, C_{Na}}{C_{Ca}^{1/2}}\right)^2\right]^2 - \left[2\left(1 + \frac{C_{Mg}}{2C_{Ca}}\right)Q_v\right]^2}}{2\left(1 + \frac{C_{Mg}}{2C_{Ca}}\right)^2} \qquad (12)$$

$$\overline{C}_{Mg,\, eq} = \overline{C}_{Ca,\, eq} \left(\frac{C_{Mg}}{2C_{Ca}}\right) \qquad (13)$$

$$\overline{C}_{Na,\, eq} = Q_v - \overline{C}_{Ca,\, eq} - \overline{C}_{Mg,\, eq} \qquad (14)$$

A set of boundary and initial conditions for each component may be expressed as

Initial Conditions

$$C_{Na}\ (x, t = 0) = (C_{Na})_{formation\ water}$$

$$C_{Ca}\ (x, t = 0) = (C_{Ca})_{formation\ water} \qquad (15)$$

$$C_{Mg}\ (x, t = 0) = (C_{Mg})_{formation\ water}$$

Boundary Conditions at the Core Entrance

$$C_{Na}\ (x = 0,\ 0 < t < t_1) = (C_{Na})_{preflood}$$

$$C_{Ca} \; (x = 0, 0 < t < t_1) = (C_{Ca})_{preflood}$$

$$C_{Mg} \; (x = 0, 0 < t < t_1) = (C_{Mg})_{preflood} \qquad (16)$$

$$C_{Na} \; (x = 0, t > t_1) = (C_{Na})_{chemical\ slug}$$

$$C_{Ca} \; (x = 0, t > t_1) = (C_{Ca})_{chemical\ slug}$$

$$C_{Mg} \; (x = 0, t > t_1) = (C_{Mg})_{chemical\ slug}$$

where t_1 is the total injection period for the preflood slug.

Boundary Conditions at the Core Exit

$$\frac{\partial C_{Na}}{\partial x} (x = L, t) = 0$$

$$\frac{\partial C_{Ca}}{\partial x} (x = L, t) = 0 \qquad (17)$$

$$\frac{\partial C_{Mg}}{\partial x} (x = L, t) = 0$$

where L is the length of the core.

III. Numerical Solution

Implicit finite difference with Gauss' elimination method was used to solve the set of equations from equations (6) through (17). The implicit finite difference form was used for each of the terms in equation (4).

$$\frac{\partial C_i}{\partial t} = \frac{C'_{i,j} - C_{i,j}}{\Delta t}$$

$$\frac{\partial C_i}{\partial x} = \frac{C'_{i,j+1} - C'_{i,j-1}}{2\Delta x}$$

$$\frac{\partial^2 C_i}{\partial x^2} = \frac{C'_{i,j+1} - 2C'_{i,j} + C'_{i,j-1}}{\Delta x^2}.$$

$i = 1, 2,$ and $3.$

where $C'_{i,j}$ denotes the concentration of the i component at the j-th interior grid point at the end of a time-step.

By substituting equation (18) into equations (6) through (14), one obtains a set of simultaneous equations in the tridiagonal matrix form for each time-step.

$$\alpha_j C'_{i,j-1} + \beta_j C'_{i,j} + \gamma_j C'_{i,j+1} = \delta_{i,j} \quad (19)$$

i = 1, 2, and 3

where

$$\alpha_j = -\left(\frac{V}{2\Delta x} + \frac{D}{\Delta x^2}\right)$$

$$\beta_j = \left(\frac{\phi}{\Delta t} + \frac{2D}{\Delta x^2}\right)$$

$$\gamma_j = \left(\frac{V}{2\Delta x} - \frac{D}{\Delta x^2}\right)$$

$$\delta_{i,j} = \frac{\phi}{\Delta t} C_{i,j} - \frac{\phi}{\Delta t} \overline{C}_{i,j}$$

During any one time-step C_i and $\overline{C}_i$ appearing in the right hand side of equation (19) are treated as constants for the tridiagonal matrix. Then, at the end of any time-step, the new C_i and $\overline{C}_i$ at all interior grid points may be obtained by solving the tridiagonal set of equations. The numerical technique is a conventional Gauss' elimination method which is discussed in details elsewhere[2,3].

IV. Parameters used in Computer Simulation

Some important parameters associated with the characteristics of the ion exchange/dispersion process are as the following.

1. Cation Exchange Capacity, Q_v

The cation exchange capacity was estimated to be 0.05 meq/ml of pore space for the laboratory core. This is approximately the median value for Berea and other sands of Mid-Continent and Gulf Coast areas. The cation exchange capacity which is associated with the type of clay on the rock surface is assumed to be constant throughout flooding process.

2. Ion Exchange Equilibrium Constants

As mentioned earlier, the equilibrium constants between Na/Ca and Ca/Mg are assumed to be 0.15 and 2.0 respectively. These values will in general depend on the type of formation and ionic composition of flooding water.

3. Ion Exchange Rate Constant, K_R

The proportional constant for the rate law of ion exchange determines the rate at which cations are transported from the rock surface to the solid-liquid interface. $K_R = 0$ implies that no ion exchange occurs between the flooding water and rocks while $K_R = \infty$ implies instantaneous equilibrium for ion exchange reactions. In this work K_R was assumed to be 50 sec^{-1} for the comparison between simulated and experimental results. This term would not affect the calculated ionic compositions much different from those assuming instantaneous equilibrium. It is not intended to discuss this term in detail.

4. Dispersion Coefficient, D

Several types of dispersion have been given in the literature. In this work the dispersion coefficient is assumed to be linearly dependent on the linear velocity[4], that is,

$$D = \lambda \cdot V \qquad (21)$$

The proportional constant λ has a unit of length. λ is a characteristic length of dispersion or simply called dispersion length. This λ may be determined by matching the calculated elution curves with those of laboratory core tests. Chloride ion, which is believed to follow the fluid front closely without any adsorption, was used as a reference tracer. For the Berea cores used in this work, the dispersion length was estimated to be one centimeter.

V. Example Calculations and Discussions

Example calculations were made by using the input data listed in Table I. Some of the calculated results were compared with experimental data. In this study, tests were conducted in 2" x 10" Berea cores which were mounted in Hassler cell. Fluids were injected through a Ruska constant volumetric pump. A sargent automatic fraction collector was used to collect the effluent solution for analysis. Calcium and total hardness (combination of calcium and magnesium) can be readily determined by standard chemical titration. Sodium ion concentration is then calculated as the difference of chloride ion concentration (determined by automatic chloride titrator) and the total hardness.

For the experiment we saturated the core with synthetic Madison water and flowed with this water until effluent composition was equal to the injected composition. We then displaced the formation water with a preflood solution. After injecting 260 cc of preflood (2.84 pore volume), a quasi-steady state composition was achieved. About 3 pore volume of simulated chemical slug (without adding any sulfonate or polymer) was then followed. The flow rate was set at 40 cc/hr. Ionic compositions of all the injected solution are listed in Table II. Three types of preflood were tested in this study to investigate the effect of preflood design on ionic composition in the front of the chemical slug. Type 1 of preflood contains 15% of formation water mixed with deionized water. In Type 2, some calculated NaCl was added to the 15% dilution of formation water to maintain for Na/Ca/Mg equilibria with the formation rock. Type 3 is a plain brine containing 1.5% salt.

1. Comparison of Experimental and Theoretical Results in the Case of Using Preflood Type 1 - 15% Formation Water

As will be seen later in this section, the divalent ions have a greater percent change than monovalent ions due to ion exchange. It was also found that calcium and magnesium ions behaved similarly. Therefore, only calcium ion concentration in effluent will be presented here to compare with experimental data. Both calculated and experimentally determined calcium ions in the effluent were normalized by calcium ions in formation water and plotted against pore volume of effluent produced. Agreement between experimental and theoretical results is only fair for the preflood/formation water displacement. This is because the end effect of the short laboratory cores. The predicted "hump" of calcium ion in the front of the chemical slug is confirmed by experiment. With this type of preflood, the slug would pick up divalent ions by ion exchange to a concentration several times greater than the injected concentration. This preflood is not desirable.

2. Comparison of Experimental and Theoretical Results in the Case of Using Preflood Type 2 - Adjusted* 15% Formation Water

As listed in Table II, the concentration ratio of sodium and calcium in the formation water is

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* $\left(\frac{Na^+}{Ca^{++}}\right)_{preflood} = \left(\frac{Na^+}{Ca^{++}}\right)_{formation\ water}$

$$\frac{C_{Na}}{C_{Ca}^{1/2}} = \frac{0.8985}{0.1392^{1/2}} \qquad (22)$$

The additional Na^+ required to obtain the properly adjusted preflood with 15% formation water may be calculated as

$$\frac{(0.15 \times 0.8985) + Na^+}{(0.15 \times 0.1392)^{1/2}} = \frac{0.8985}{0.1392^{1/2}} \qquad (23)$$

or $Na^+ = 0.2132$ meq/ml

By the addition of 0.2132 meq/ml of Na^+ into preflood 1, the ratios of Na^+ to Ca^{++} in preflood and formation water are equal (balanced). In this case, there is no ion exchange between the flood water and the formation rock. Simulated and experimentally determined calcium in effluent were compared in Figure 2. As we expected, the calcium ion concentration did not increase in the chemical slug/preflood displacement. Agreement between experimental and calculated composition is good. Such a preflood would not change the reservoir rock property, and no ion exchange would occur during the preflush. This design is recommended because of its simplicity in predicting the preflood performance without knowing the ion exchange characteristics of the rocks.

3. Comparison of Experimental and Theoretical Results in the Case of Using Preflood Type 3 - 1.5% NaCl

In this test, on plain brine containing 1.5% NaCl was used as the preflood. Figure 3 shows that good agreement between experimental and simulated results is again achieved for the chemical slug/preflood displacement. Equation (1) indicated that if the Na/Ca ratio in flooding water is increased, the Na/Ca ratio on clays will be also increased in order to maintain equilibrium. The chemical slug, following the preflood, will then equilibrate with