Dynamic Interfacial Tensions in Acidic Crude Oil/Caustic Systems

Part II: Role of Dynamic Effects in Alkaline Flooding for Enhanced Oil Recovery

A model for caustic propagation in a core during continuous injection is combined with the considerations of interfacial reactions proposed in Part I in order to examine the role of dynamic effects in continuous alkaline flooding. Axial dispersion of caustic and its reversible uptake by the reservoir rock are taken into account. From this model, the interfacial tension between an isolated oil globule and the surrounding flood water can be predicted as a function of time using the knowledge of the kinetics of interfacial reactions, the rock adsorption equilibria, and the longitudinal dispersion coefficient.

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SCOPE

The interfacial tension between acidic crude oil and caustic, when freshly contacted in a spinning drop tensiometer, changes continuously with time until the equilibrium is established, often displaying a dramatic minimum value in short times. In Part I, by proposing a set of interfacial reactions a chemical diffusion-kinetic model was developed. The model was utilized for determining the rate constants of the interfacial reactions from a correlation of experimental data. In this paper we attempt to examine the behavior of this acidic oil/caustic system under flow conditions encountered during a continuous alkaline flood.

A simple model for caustic propagation in a core during its continuous injection is combined with the considerations of interfacial reactions which lead to *in situ* generation of surfactants. Since the saponification product partitions preferentially into the oil phase, the multiple-contact interfacial tensions achieved are close to those of first contact (Borwankar, 1984). Thus, since only very small amounts of the acid are extracted into the aqueous phase even after repeated contacts with the alkali, transport of surfactant to the aqueous phase can be neglected. Axial dispersion of caustic and its reversible uptake by the reservoir rock are taken into account.

Adsorption on the rock causes a delay in the elution of caustic, while axial dispersion causes blurring of the caustic front. This blurring is unopposed in the case of a linear isotherm governing the adsorption on the rock and increases with distance. The self-sharpening effects of Langmuirian adsorption, on the other hand, lead to the formation of a steady front which, once established, propagates at a uniform velocity. An unsteady state solution is obtained for the case of a linear isotherm while a steady state (long time) solution is obtained for the Langmuirian case. Only single-phase flow is considered.

Using this model, the oil/water interfacial tensions in the core can be predicted as a function of time from the knowledge of the kinetics of the interfacial reactions. The importance of the nonequilibrium effects can then be assessed by comparison with the equilibrium case.

Earlier deZabala and Radke (1982) examined the problem of the importance of nonequilibrium effects in alkaline flooding, but for simple physical transport of surfactant across the interface. They also did not

account for axial dispersion. Hirasaki (1980) considered a similar problem with axial dispersion effects but without the self-sharpening effects of adsorption. In the model developed here the self-sharpening effects of Langmuirian adsorption are examined. More importantly, the present model is a chemical model and utilizes the more realistic system chemistry proposed recently by Ramakrishnan and Wasan (1983).

CONCLUSIONS AND SIGNIFICANCE

Adsorption on the rock causes a chromatographic lag in the elution of caustic. The axial dispersion causes the caustic concentration in the flood water surrounding an isolated oil globule in the core to change gradually from zero to injection levels. The caustic propagation equations are solved together with surfactant generation equations in order to assess the role of dynamic effects.

The model developed herein permits a prediction of interfacial tension between an isolated oil globule and the surrounding aqueous phase in oil-bearing rock. For over-optimum levels of injected caustic, the interfacial tension passes through a minimum and then rises to a final value that corresponds to the equilibrium measurements in the spinning drop tensiometer.

The blurring of the caustic front is unopposed in the case of a linear isotherm governing the caustic adsorption on the rock and increases with distance. In short cores, the minimum interfacial tension is influenced by the nonequilibrium effects and is higher or lower than the equilibrium case depending on the relative extent of the adsorption/desorption barriers. Dispersion over longer distances, however, would cause long cores and field projects to be in chemical equilibrium.

For the Langmuir isotherm, on the other hand, the blurring of the caustic front due to axial dispersion is opposed by the self-sharpening effects due to the convexity of the isotherm and a steady state is finally reached. The steady front, once established, propagates uniformly with a characteristic velocity governed by the isotherm chord. The steady front may be such that the concentration changes are rapid enough for nonequilibrium effects to be important even under field conditions. From the knowledge of the rate constants of the interfacial reactions, the dynamic interfacial tension between the trapped oil and the flood water can be predicted.

The establishment of the steady state implies that oil recovery observed in laboratory studies conducted on sufficiently long cores would correspond directly to that possible in oil fields. A further implication is that the final value of the interfacial tension, which corresponds to the equilibrium value in the spinning drop tensiometer, should govern the displacement of connected oil. For over-optimum systems, the transient minimum should apply to mobilization of the disconnected oil blobs.

Introduction

In Part I of this two-part series, a chemical diffusion-kinetic model was developed for surfactant transport in the acidic oil/caustic system of alkaline flooding. This model was used to correlate the dynamic interfacial data obtained using the spinning drop interfacial tensiometer for one such system. The kinetic parameters in the model could be obtained by correlating the experimental data. In this paper we will use this information to assess the role of dynamic effects in continuous alkaline flooding. The attention will be focused on caustic flooding.

Acidic crude oil/caustic systems often show a dramatic dynamic interfacial tension minimum followed by a slow rise to equilibrium values (McCaffery, 1976; Chan, 1978; Rubin and Radke, 1980; Trujillo, 1983; Borwankar, 1984). deZabala and Radke (1982) constructed a simple model for a continuous alkaline flood. From considerations that the surfactant is predominantly partitioned into the aqueous phase, they showed that the multiple contact interfacial tension is achieved, with the interfacial tension approaching the one corresponding to equilibrium between aqueous surfactant and the oil at its original acid number. The presence of large adsorption/desorption barriers may then cause drastic departures from the equilibrium displacement, and consequently tertiary flooding tests in the laboratory may underestimate the oil recovery possible in a field application (deZabala and Radke).

A similar conclusion, that nonequilibrium effects may be significant in laboratory core floods but not in field projects, was reached by Hirasaki (1980) for surfactant flooding, but from a different standpoint. By considering longitudinal dispersion in the absence of self-sharpening effects of adsorption, he showed that the concentration changes may be rather rapid in short cores; but dispersion over longer distances in a field project causes slower concentration changes. Thus, a field project would more likely be in chemical equilibrium.

From this brief discussion it is apparent that in the context of the system chemistry of Ramakrishnan and Wasan (1983), the theory of continuous alkaline flooding should be reexamined. Specifically, since the saponification products partition preferentially into the oil phase, the multiple-contact interfacial tensions achieved are close to those at first contact (Borwankar, 1984). The theory of deZabala and Radke is not applicable to this case. A model of a continuous alkaline flood based on the system chemistry proposed by Ramakrishnan and Wasan is developed. The nonequilibrium effects are incorporated from considerations of the kinetics of interfacial reactions following the approach adopted in Part I. Effects of axial (longitudinal) dispersion are examined. The model is constructed with a view to provide a basis for scale-up of oil recovery determinations from laboratory tests to predictions in a field operation. The model also provides an insight into the interfacial tension that may be applicable during alkaline flooding.

Another aspect of caustic flooding incorporated in the model is the caustic uptake by the reservoir rock. The consumption of caustic by the reservoir rock occurs by both reversible and irreversible processes (Sydansk, 1982; Bunge, 1982). We shall focus our attention on reversible sodium/hydrogen-base ion exchange. The reaction is considred to be fast and causes a delay in the elution of caustic (deZabala and Radke, 1982; Radke and Somerton, 1982). The reaction may be represented as (Bunge, 1982):

$$\overline{M}H + Na^+ + OH^- \rightleftharpoons \overline{M}Na + H_2O \tag{1}$$

where $\overline{M}$ denotes a mineral-base exchange site. For Wilmington Field sand, Radke and Somerton have reported the isotherm governing this exchange to be of Langmuir type with hydrogen exchange capacity of about 100 meq/100 g of sand. We shall take the reversible caustic consumption by the above reaction into account in the flow model. In particular, the consequences of the self-sharpening effect of the Langmuir isotherm will be addressed.

Continuous Flow Model

Description of the model

A schematic diagram of the system under consideration is shown in Figure 1. Initially the oil-bearing rock contains isolated oil globules trapped in its pores. These oil globules are surrounded by saline water from the preceding water flooding. The caustic flood is begun by injecting caustic solution (of the same salinity as the water flood) at a steady rate at the core inlet. The caustic propagates through the core and some of it is adsorbed on the rock. In the absence of axial dispersion the caustic would propagate as a step moving through the core at a characteristic velocity (deZabala and Radke). Thus, an isolated oil globule which is located a certain distance into the core would see a step change in caustic concentration when the front arrives there. However axial dispersion causes the caustic concentration around the oil globule to rise gradually from the initial zero value to the injection alkali concentration.

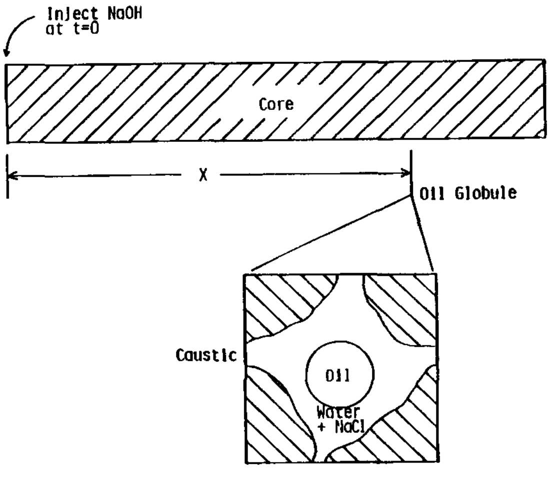

Figure 1. Schematic diagram of system, showing an oil globule trapped in a pore of oil-bearing core.

The problem of caustic propagation is complicated by the fact that, in general, two-phase flow takes place in the core and significant capillary dispersion should occur. Thus, fractional flows as functions of saturation must be used to solve this problem (Ramakrishnan, 1985; deZabala *et al.*, 1982). Nonequilibrium effects may then be incorporated in terms of mass transfer resistances and kinetics of interfacial reactions. However, the problem then becomes formidable. To assess the importance of dynamic effects in the presence of axial dispersion, a model is developed here to predict the dynamic interfacial tension between a single oil globule and the surrounding aqueous phase. Thus, the water saturation is effectively unity and only single-phase flow is considered.

Caustic propagation

With a water saturation of unity, the caustic propagation in the flowing aqueous phase obeys the equation (Rachinskii, 1965)

$$\phi \frac{\partial C_{OH}}{\partial t} + (1-\phi)\frac{\partial n_{OH}}{\partial t} + v\frac{\partial C_{OH}}{\partial x} = D_L \frac{\partial^2 C_{OH}}{\partial x^2}; \tag{2}$$

where ϕ is the porosity of the medium, v is the superficial velocity of the aqueous phase, D_L is the axial dispersion coefficient in the single-phase flow, and C_{OH} and n_{OH} are concentrations of caustic in the flowing aqueous phase and the reservoir rock respectively. The use of D_L as a single-phase dispersion coefficient ignores the alteration of streamlines due to the presence of the isolated heterogeneity. Furthermore, the use of the above equation neglects the consumption of caustic during *in situ* generation of surfactant.

The isotherm governing the reversible uptake of caustic by the reservoir rock is represented in the general form

$$n_{OH} = f(C_{OH}). \tag{3}$$

The adsorption process is assumed to be fast and, thus, adsorption equilibrium exists.

The initial condition is given by

$$\begin{aligned} C_{OH}(0,0) &= C_0, \\ C_{OH}(x,0) &= 0, \qquad x > 0. \end{aligned} \tag{4}$$

The boundary conditions are given by

$$C_{OH}(0,t) = C_0, \qquad t > 0 \tag{5}$$

$$\lim_{x\to\infty} C_{OH}(x,t) = 0, \qquad t > 0. \tag{6}$$

Surfactant generation

The surfactant is generated *in situ* by neutralization of acids in the crude oil by the caustic (Ramakrishnan and Wasan, 1983). Experimental evidence suggests that very little surfactant is extracted into the aqueous phase even after repeated contacts of the caustic solution with the oil (Borwankar et al., 1984). Therefore, in this model the transport of the surfactant to the aqueous phase is neglected. The mechanism of surfactant

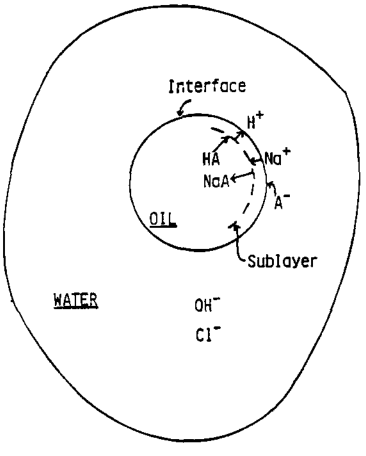

Figure 2. Surfactant generation mechanism.

generation is depicted schematically in Figure 2. Again, the various acids in the crude oil are represented by a single component HA with average properties. The system chemistry of surfactant generation that is used here was proposed by Ramakirshnan and Wasan and is also discussed in detail in Part I. The anion A^- is assumed to be the only adsorbable species. Molecular diffusion governs the transport of the acid HA and the neutralization product, soap NaA, in the oil globule. For the case of a spherical oil globule,

$$\frac{\partial C_{HA_o}}{\partial t} = D_{HA_o}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{HA_o}}{\partial r}\right) \tag{7}$$

and

$$\frac{\partial C_{NaA_o}}{\partial t} = D_{NaA_o}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{NaA_o}}{\partial r}\right). \tag{8}$$

Initially, the acid is uniformly distributed in the oil globule and the soap is absent; thus,

$$C_{HA_o}(r, 0) = C^0_{HA_o}, \tag{9}$$

$$C_{NaA_o}(r, 0) = 0. \tag{10}$$

The various interfacial reactions together with their kinetics have been discussed in Part I. These give the boundary conditions at the interface to be

$$-D_{HA_o}\frac{\partial C_{HA_o}}{\partial r}\bigg|_s = k_{HA}\left[C^s_{HA_o}(\Gamma_\infty - \Gamma) - \frac{\Gamma}{K_{HA}}C_{H^+}\exp\left(-\frac{F\psi_0}{RT}\right)\right] \tag{11}$$

and

$$-D_{NaA_o}\frac{\partial C_{NaA_o}}{\partial r}\bigg|_s = k_{NaA}\left[C^s_{NaA_o}(\Gamma_\infty - \Gamma) - \frac{\Gamma}{K_{NaA}}C_{Na^+}\exp\left(-\frac{F\psi_0}{RT}\right)\right], \tag{12}$$

where the concentrations C_{H^+} and C_{Na^+} are now varying with time as governed by the caustic propagation equations.

Finally, species balance at the interface is given by

$$\frac{d\Gamma}{dt} = -D_{HA_o}\frac{\partial C_{HA_o}}{\partial r}\bigg|_s - D_{NaA_o}\frac{\partial C_{NaA_o}}{\partial r}\bigg|_s. \tag{13}$$

Note that this does not account for the transfer to the aqueous phase.

Equations 7–13 can be solved once the problem of caustic propagation is solved, since the concentrations C_{Na^+} and C_{H^+} are varying with time at the location of the oil globule.

Method of solution

The solution to the problem of caustic propagation is strongly dependent on the nature of the adsorption isotherm represented by Eq. 3. The case of a concave isotherm is not of significance here. For the sake of completeness, it suffices to say that in this case the blurring of the caustic front occurs due to both axial dispersion and the concavity of the isotherm.

For the case of a linear isotherm the blurring of the front occurs only due to axial dispersion. Exact solution is very complex and only an approximate solution is discussed.

In the case of a convex isotherm, the blurring of the caustic front occurs due to axial dispersion but is opposed by compression of the front due to the convexity of the isotherm (Rachinskii, 1965). The compression of the front by the convex adsorption isotherms causes what was referred to earlier as the self-sharpening effect. These two processes eventually exactly cancel each other and a steady state is reached. The blurred front propagates at a uniform velocity once the steady state is reached. To evaluate the time of formation of the steady state front is a formidable task and only the steady state solution is discussed. This case is of particular interest here since the Langmuir isotherm, which was shown to apply for Wilmington Field sand, falls into this category (Radke and Somerton, 1982).

Linear Isotherm. An approximate solution to the problem of caustic propagation with a linear adsorption isotherm is obtained by replacing the boundary condition of Eq. 5 by (Smith, 1981)

$$\lim_{x\to-\infty} C_{OH}(x, t) = C_0 \tag{14}$$

and the initial condition of Eq. 4 by

$$C_{OH}(x, 0) = 0, \qquad -\infty < x < \infty. \tag{15}$$

For the linear isotherm represented by

$$n_{OH} = KC_{OH} \tag{16}$$

Eq. 2 governing caustic propagation becomes

$$[\phi + K(1-\phi)]\frac{\partial C_{OH}}{\partial t} + v\frac{\partial C_{OH}}{\partial x} = D_L\frac{\partial^2 C_{OH}}{\partial x^2}. \tag{17}$$

Defining

$$u = \frac{v}{\phi + K(1-\phi)} \tag{18}$$

and

$$D^* = \frac{D_L}{\phi + K(1 - \phi)}, \tag{19}$$

Eq. 17 becomes

$$\frac{\partial C_{OH}}{\partial t} + u\frac{\partial C_{OH}}{\partial x} = D^* \frac{\partial^2 C_{OH}}{\partial x^2}. \tag{20}$$

Solution of Eq. 20, with Eq. 15 as initial condition and Eqs. 6 and 14 as boundary conditions, is given by

$$\frac{C_{OH}}{C_0} = 0.5\left[1 - \mathrm{erf}\left(\frac{x - ut}{\sqrt{2D^*t}}\right)\right]. \tag{21}$$

Once the caustic concentration at the location of the globule is known, the system Eqs. 7–13 can be solved. Equations 7 and 8 are set in the finite-difference form using the Crank-Nicholson scheme. The trapezoidal rule is applied to Eq. 13. Again the interfacial boundary conditions make the system nonlinear. Thus, the secant method is used to iterate on Γ. Once Γ is assumed as a guess, these equations become linear. The Thomas algorithm (Finlayson, 1980) is used to solve the finite-difference equations. The solution yields Γ as a function of time and, using the equation of state, interfacial tension as a function of time is calculated. The detailed procedure is discussed by Borwankar (1984).

Convex Isotherm. The steady state solution for the caustic propagation Eqs. 2–6 can be obtained for the case of a convex isotherm. At steady state the blurring due to axial dispersion is exactly canceled by the compression of the front due to the convexity of the isotherm. The blurred front then propagates uniformly through the core at a constant velocity. It is necessary to determine the shape of the blurred front and the characteristic velocity of the front.

Let u be the characteristic velocity with which the blurred front propagates through the medium. Then, defining a new variable

$$z = x - ut, \tag{22}$$

it is possible to travel with the blurred front. In terms of this new variable, the steady state propagation of caustic is governed by

$$-\phi u \frac{dC_{OH}}{dz} + v\frac{dC_{OH}}{dz} - (1 - \phi)u\frac{dn_{OH}}{dz} = D_L \frac{d^2C_{OH}}{dz^2}. \tag{23}$$

Since steady state is under consideration, the initial condition represented by Eq. 4 drops out and the boundary conditions, Eqs. 4 and 5 in terms of the new variable become

$$\lim_{z\to -\infty} C_{OH} = C_0 \tag{24}$$

and

$$\lim_{z\to\infty} C_{OH} = 0. \tag{25}$$

Integration of Eq. 23 yields

$$-\phi u C_{OH} + vC_{OH} - (1 - \phi)un_{OH} = D_L \frac{dC_{OH}}{dz} + \lambda_1$$

or

$$-\phi u C_{OH} + vC_{OH} - (1 - \phi)uf(C_{OH}) = D_L \frac{dC_{OH}}{dz} + \lambda_1. \tag{26}$$

The boundary condition represented by Eq. 25 also implies that

$$\lim_{z\to\infty} \frac{dC_{OH}}{dz} = 0$$

and knowing $f(0) = 0$, application of this boundary condition gives $\lambda_1 = 0$, thus

$$-\phi u C_{OH} + vC_{OH} - (1 - \phi)uf(C_{OH}) = D_L \frac{dC_{OH}}{dz}. \tag{27}$$

Similarly, the boundary condition represented by Eq. 24 also implies

$$\lim_{z\to -\infty} \frac{dC_{OH}}{dz} = 0$$

and application of this boundary condition gives the velocity of the steady state front:

$$u = v\frac{C_0}{\phi C_0 + (1 - \phi)f(C_0)}. \tag{28}$$

It is seen from Eq. 28 that the characteristic velocity of propagation of the steady front is governed by the ratio $f(C_0)/C_0$ which is the slope of the isotherm chord. For a convex isotherm this means that decreasing the injected concentration decreases the characteristic velocity at which the steady blurred front propagates.

The caustic concentration can be found by integrating Eq. 27; thus,

$$z + \lambda_2 = \frac{D_L}{(1 - \phi)u} \int \frac{dC_{OH}}{\left[\frac{f(C_0)}{C_0} C_{OH} - f(C_{OH})\right]}, \tag{29}$$

where λ_2 is the new integration constant. This integration constant cannot be determined from the steady state considerations.

Consider the Langmuir isotherm which is of special interest here:

$$\frac{n_{OH}}{n_\infty} = \frac{KC_{OH}}{1 + KC_{OH}}, \tag{30}$$

where K and n_∞ are the isotherm constants, n_∞ being the satura-

tion adsorption. For this case the characteristic velocity is

$$u = \frac{v}{\left[\phi + (1-\phi)\dfrac{Kn_\infty}{1+KC_0}\right]} \tag{31}$$

and the caustic concentration is given by

$$z + \lambda_2 = \frac{D_L}{(1-\phi)u}\int \frac{dC_{\mathrm{OH}}}{\left[\dfrac{Kn_\infty C_{\mathrm{OH}}}{1+KC_0} - \dfrac{Kn_\infty C_{\mathrm{OH}}}{1+KC_{\mathrm{OH}}}\right]}$$

or

$$z + \lambda_2 = \frac{D_L}{(1-\phi)u}\int \frac{(1+KC_0)(1+KC_{\mathrm{OH}})}{Kn_\infty C_{\mathrm{OH}}(C_{\mathrm{OH}} - C_0)}\, dC_{\mathrm{OH}}. \tag{32}$$

Defining

$$\gamma = \frac{Kn_\infty}{1+KC_0}\,\frac{1-\phi}{\phi}, \tag{33}$$

Eqs. 31 and 35 can be written as

$$u = \frac{v}{\phi(1+\gamma)} \tag{34}$$

and

$$z + \lambda_2 = \frac{D_L}{v}\,\frac{1+\gamma}{\gamma}\int \frac{1+KC_{\mathrm{OH}}}{C_{\mathrm{OH}}(C_{\mathrm{OH}} - C_0)}\, dC_{\mathrm{OH}}. \tag{35}$$

Integration of Eq. 35 yields

$$(1+KC_0)\ln\left(1 - \frac{C_{\mathrm{OH}}}{C_0}\right) - \ln\left(\frac{C_{\mathrm{OH}}}{C_0}\right) = \frac{\gamma}{1+\gamma}\,\frac{v}{D_L}(z+\lambda_2)$$

or

$$(1+KC_0)\ln\left(1 - \frac{C_{\mathrm{OH}}}{C_0}\right) - \ln\left(\frac{C_{\mathrm{OH}}}{C_0}\right) = \frac{\gamma}{1+\gamma}\,\frac{v}{D_L}(x - ut + \lambda_2). \tag{36}$$

Thus, the caustic concentration at the location of the globule is known to an arbitrary constant; the blurred front propagates at a constant velocity. This arbitrariness in solution does not pose any problem. The surfactant generation equations can now be solved in the same manner as for the case of a linear isotherm (see Borwankar, 1984). Again, the solution yields the surfactant concentration as a function of time, from which the interfacial tension can be obtained as a function of time using the equation of state.

Results and Discussion

Computer calculations were performed using the continuous flow model to study the effects of the various parameters. The equilibrium constants used in the parametric study are the same as those given earlier (Table 1 of Part I) for Wilmington Field (C–331) crude oil, but the caustic concentration in the aqueous phase is now the injected caustic concentration, C_0. Since the surfactant transport to the aqueous phase is justifiably neglected, the final values predicted by the model correspond to the equilibrium values measured in the spinning drop tensiometer for caustic concentration at injected levels.

The other parameters used in the parametric study are given in Table 1. The parameters are typical of an alkaline water flood, although as mentioned above, the water saturation is unity. As pointed out in Part I, the diffusivities in the oil phase are assumed to be so small primarily because the oil is highly viscous (100–110 mPa·s at room temperature).

Linear isotherm

Computer calculations for the case of linear isotherm were performed using the unsteady state solution for caustic propagation. The results are dependent on the distance of the oil globule from the core inlet.

Figure 3 shows the variation of interfacial tension when the oil globule is at a distance of 10 cm from the core inlet. The axial dispersion causes the caustic concentration in the aqueous phase surrounding the oil globule to change with time. The variation of caustic concentration around the oil globule is shown in the figure by the dashed line. In order to assess the importance of the dynamic effects, the equilibrium case was studied for the purpose of comparison. In the equilibrium case, the interfacial concentration, and hence the interfacial tension, is in equilibrium with the caustic concentration in the surrounding aqueous phase. As the caustic concentration changes, the interfacial tension in equilibrium with it also changes as shown by curve 3. Since the equilibrium interfacial tension vs. caustic concentration curve passes through a minimum in batch systems (Ramakrishnan and Wasan, 1983), the interfacial tension of the trapped oil globule also displays a minimum.

Curves 1 and 2 of Figure 3 show the interfacial tension in the presence of dynamic effects. It is seen that the minimum interfacial tension may be higher or lower than in the equilibrium case, depending on the values of the rate constants. This can be explained by referring to the two extreme cases. The equilibrium case shown here corresponds to the case of an infinite axial dispersion coefficient for any combination of the rate constants. On the other extreme, the batch system of Part I corresponds to the case of zero axial dispersion. Therefore, the minimum inter-

Table 1. Constants Used in the Parametric Study

Parameter	Symbol	Value
Porosity	ϕ	0.3
Superficial velocity	v	1.0×10^{-5} m/s
Diffusivity in oil	$D_{\mathrm{NaA}_O}, D_{\mathrm{HA}_O}$	5.0×10^{-12} m^2/s
Axial dispersion coefficient	D_L	1.0×10^{-9} m^2/s
Oil globule radius		50 μm
	Linear Isotherm	
Isotherm Constant	K	0.07
	Langmuir Isotherm	
Isotherm constant	K	0.15 m^3/mol
Isotherm constant	n_∞	18.333 mol/m^3

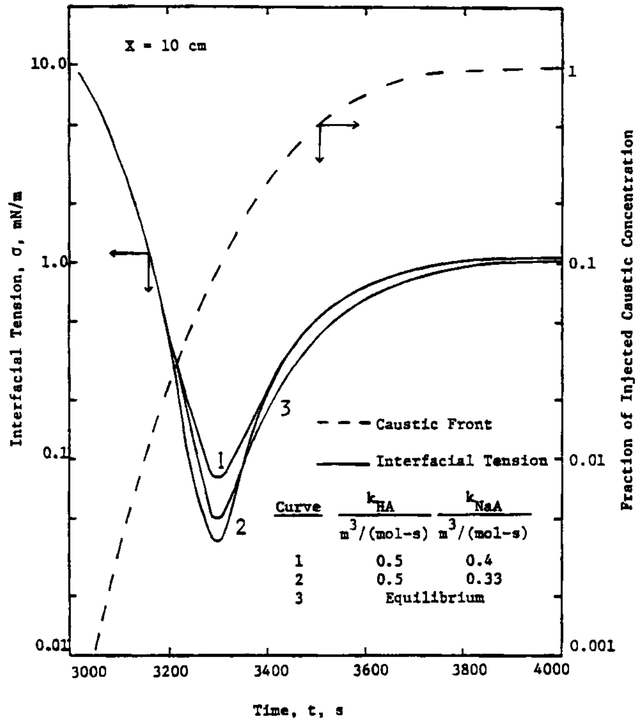

Figure 3. Blurred caustic front and interfacial tension variation for linear rock adsorption isotherm. Injected caustic concentration 250 mol/m^3, salinity 170 mol/m^3.

facial tension for the given values of rate constants should always be between the minimum equilibrium value and the minimum value under batch conditions for these rate constants. The values of the rate constants used to obtain curve 1 were found to yield a minimum under batch conditions which is higher than the minimum equilibrium value; those for curve 2 yielded lower.

Figure 4 shows the minimum interfacial tension achieved in the presence of dynamic effects as a function of the location of the oil globule. The blurring of the caustic front due to the axial dispersion increases as the front propagates through the core. It is therefore to be expected that the dynamic effects will be less and less important as the distance into the core increases. This is in fact observed from Figure 4 wherein the minimum interfacial tension in the presence of dynamic effects approaches the minimum equilibrium value with increasing distance. This confirms the applicability to caustic flooding of the conclusion reached by Hirasaki (1980) in the case of surfactant flooding, namely, whereas the nonequilibrium effects may be important in short laboratory cores, dispersion over longer distances in the absence of self-sharpening effects of adsorption causes equilibrium to exist in a field project.

Langmuir isotherm

Computer calculations for the case of a Langmuir isotherm were performed using the steady state solution for caustic propagation. This isotherm falls into the category of convex isotherms for which increasing the injected concentration leads to a higher characteristic velocity of propagation. The convex isotherm for adsorption on the reservoir rock should be a more realistic case in alkaline flooding. The Langmuir isotherm constants in Table 1 were chosen to fit the data of Radke and Somerton (1982) for Wilmington field sand. Since the solution is for the steady state, the curves are independent of the location of the oil globule in the core. Also, the time is known only to an arbitrary constant. Thus, in Figures 5–8 the origin of the time axis is chosen arbitrarily.

Figure 5 shows the oil/water interfacial tension in the core along with the blurred caustic front at steady state. The dashed

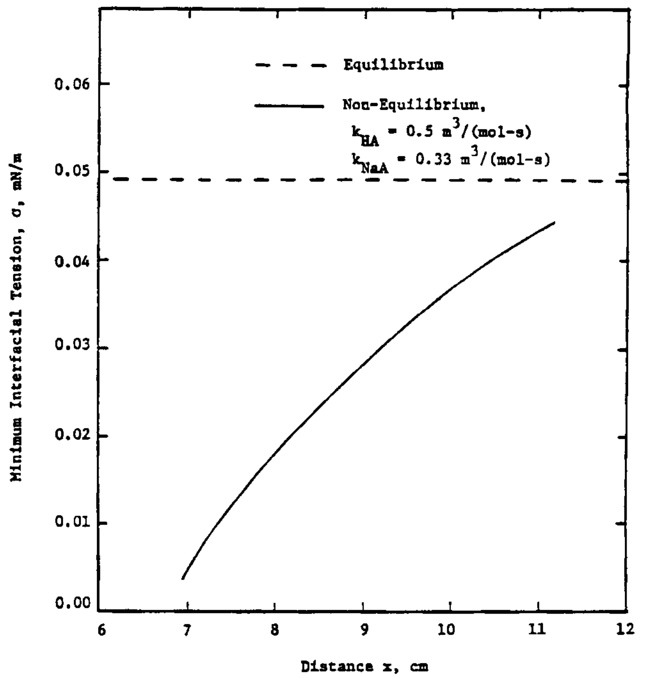

Figure 4. Variation of minimum interfacial tension with distance for linear rock adsorption isotherm in the presence of non-equilibrium effects.

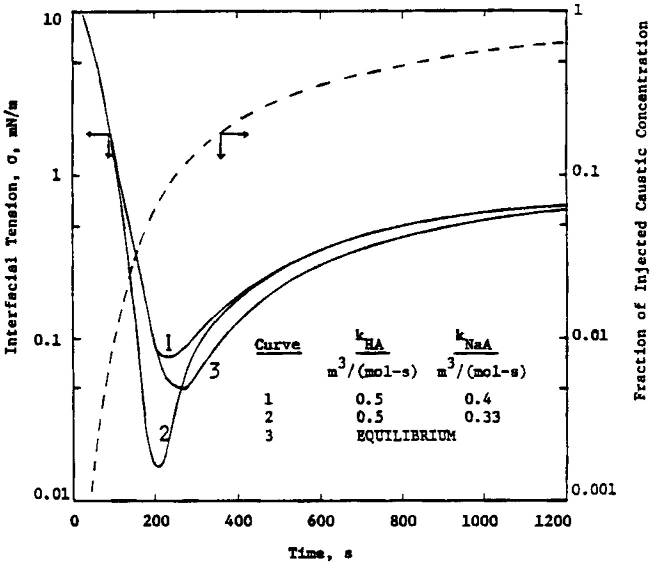

Figure 5. Blurred caustic front at steady state and interfacial tension variation for Langmuir rock adsorption isotherm. Injected caustic concentration 250 mol/m^3, salinity 170 mol/m^3.

curve shows the blurred caustic front and the solid lines show the interfacial tension. Again, the equilibrium case is shown for comparison purposes (curve 3). Curves 1 and 2 show the interfacial tension in the presence of dynamic effects. It is again seen that, depending on the values of the rate constants, the interfacial tension minimum in the presence of the dynamic effects can be higher or lower than the equilibrium case. An increase of the desorption barrier (from an initially low value) thus causes the minimum interfacial tension to change from a value higher than the minimum in the equilibrium case to one lower than it.

The case shown in Figure 5 was for an injected alkali concentration greater than that which gives the lowest equilibrium interfacial tension in batch systems, or what may be called an over-optimum system (by analogy with the systems involved in surfactant flooding). Figure 6 shows the case of optimum system, i.e., one in which the injected alkali concentration is about that corresponding to the minimum equilibrium interfacial tension. At this injected alkali concentration, the equilibrium case does not show a minimum (dashed line). In the presence of dynamic effects, however, a minimum is observed depending on the extent of the desorption barriers (curves 1 and 2). Lowering of the injected alkali concentration by a factor of 10 also causes the characteristic velocity of propagation of the steady blurred front to decrease by a factor of about 3.7.

The model developed here can be used to predict oil/water interfacial tensions during continuous alkaline flooding from the knowledge of interfacial reaction kinetics, rock adsorption equilibria and longitudinal dispersivity. In Part I, we have characterized the kinetics of interfacial reactions for Wilmington field crude oil. Adsorption equilibria for Wilmington field sand have been studied by Radke and Somerton. It is assumed that the single-phase dispersion coefficient is close to the molecular diffusion coefficient. Figures 7 and 8 show the model predictions for this system for two injected alkali concentrations. The rate constants used for the nonequilibrium case are those obtained in

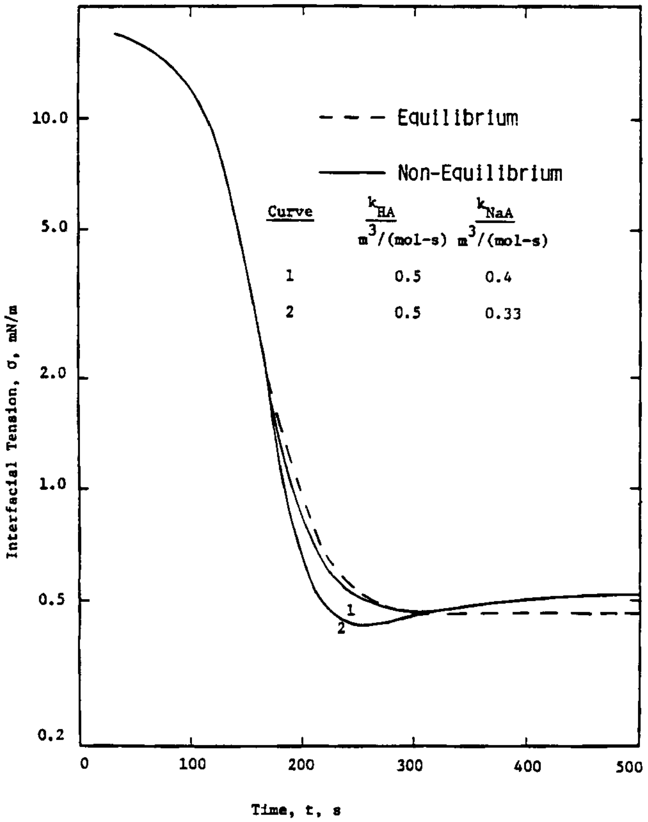

Figure 6. Interfacial tension variation for Langmuir rock adsorption isotherm. Injected caustic concentration 25 mol/m^3, salinity 170 mol/m^3.

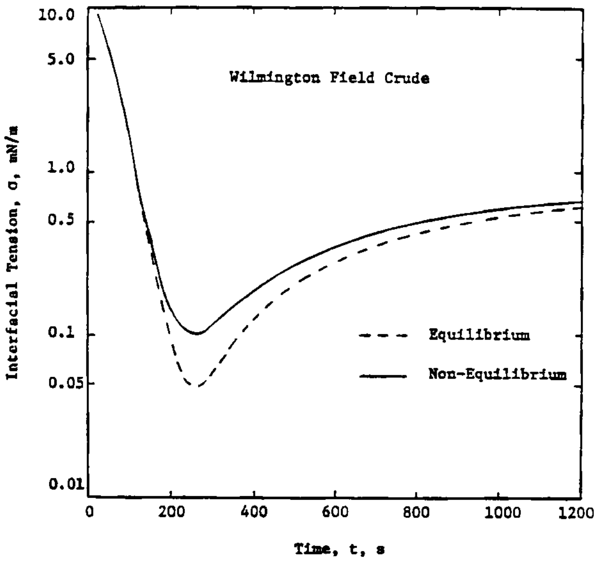

Figure 7. Interfacial tension of Wilmington Field crude oil against aqueous phase. Injected caustic concentration 250 mol/m^3, salinity 170 mol/m^3.

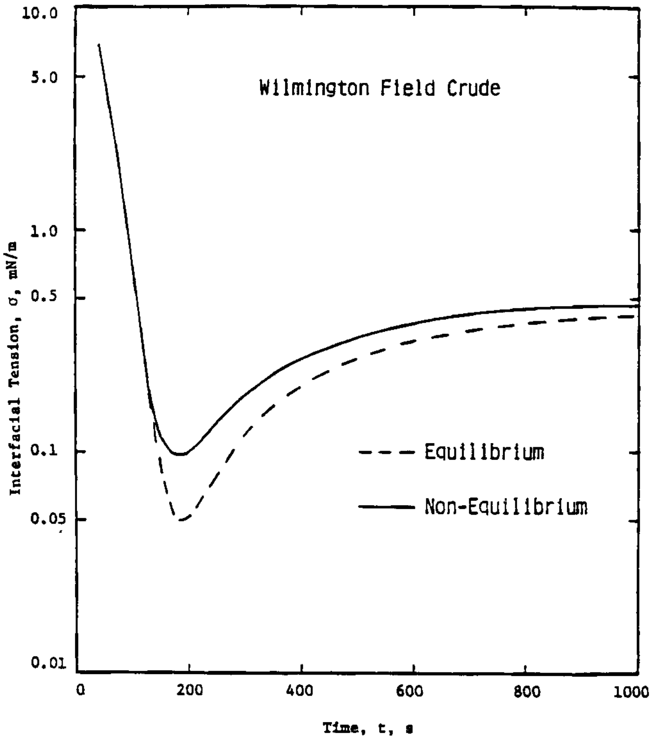

Figure 8. Interfacial tension of Wilmington Field crude oil against aqueous phase. Injected caustic concentration 125 mol/m^3, salinity 170 mol/m^3.

Part I from a correlation of the dynamic interfacial tension data and the other parameters are the same as in Table 2 of Part I. The dashed lines show the equilibrium cases for comparison purposes. It is seen that the nonequilibrium effects may cause the minimum interfacial tensions to be higher than in the equilibrium case.

Implications

The foregoing continuous flow model permits a prediction of interfacial tension between the oil globule and the surrounding aqueous phase in oil-bearing sandstone. The model is for the case of single-phase flow only, although the formation of a steady caustic front should be observed in the case of multiphase flow also. To predict the interfacial tension history, however, the complete multiphase flow problem would have to be solved.

Blurring of the caustic front occurs due to axial dispersion of caustic. In the blurred front the caustic concentration changes gradually from zero to injection levels. In the case of a linear isotherm continuous blurring of the front occurs. Dispersion over longer distances would, therefore, cause long cores and field projects to be in chemical equilibrium. At equilibrium, the interfacial tension changes with time as the caustic concentration in the flood water surrounding the oil globule changes gradually.

In the case of the Langmuir isotherm, the blurring of the caustic front is opposed by the self-sharpening effects of adsorption on the rock, and a steady state is finally established. The steady front, once established, travels with a uniform velocity, (i. e., without further blurring), governed by the isotherm chord. The steady front may be such that the caustic concentration in the flood water may change sufficiently rapidly for the nonequilibrium effects to be important. The establishment of the steady front suggests that laboratory core flooding experiments should be conducted in cores of increasing lengths. For long enough cores, where steady state is established within a relatively small distance from the inlet, the oil recovery should be unaffected by any further increase in length. The oil recovery from such cores may then correspond to that observed in fields, other things such as sweep efficiency being equal. The core flooding results for continuous alkali injection in such long cores would then directly apply at field scales. While it is not possible to theoretically predict how long the core should be for this purpose without solving the unsteady problem, it could be determined from experiments with cores of increasing lengths.

The propagation velocity of the steady caustic front increases with the injection concentration of caustic. In order to maintain reasonable propagation velocities, high injection concentrations must be used and, thus, usually over-optimum levels of injection are encountered. The model predicts that a transient interfacial tension minimum should occur for continuous injection of over-optimum levels of caustic. In the presence of nonequilibrium effects, this minimum value may be either higher or lower than in the equilibrium case. The interfacial tension rises after the minimum to the final value, which corresponds to the equilibrium interfacial tension between the oil and the aqueous phase containing injection levels of caustic as measured in the batch experiments such as in the spinning drop tensiometer. The minimum value should apply to mobilization of the disconnected oil blobs but the final value applies for the displacement of connected oil. The improved displacement efficiency can be achieved by using near optimum levels of caustic, but, as is seen above, the frontal advance rates are greatly reduced in the process. Nelson (1984) has recently proposed the use of cosurfactant-enhanced alkaline flooding to overcome this dilemma.

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Notation

C_0 = injected concentration of caustic, mol/m^3
C_i = concentration of i, mol/m^3
D_i = diffusivity of i, m^2/s
D_L = axial dispersion coefficient, m^2/s
D^* = dispersion coefficient, Eq. 19, m^2/s
F = Faraday constant, C/mol
k_{HA} = rate constant for adsorption of HA from oleic sublayer, m^3/mol·s
k_{NaA} = rate constant for adsorption of NaA from oleic sublayer, m^3/mol·s
K = equilibrium constant for adsorption of caustic on the reservoir rock
K_{HA} = equilibrium constant for HA adsorption from oleic sublayer
K_{NaA} = equilibrium constant for NaA adsorption from oleic sublayer
n_{OH} = concentration of adsorbed caustic, mol/m^3
n_∞ = saturation adsorption of caustic on the reservoir rock, mol/m^3
r = radial coordinate, m
R = gas constant, J/mol·K
t = time, s
T = temperature, K
u = characteristic velocity of propagation of the caustic front, m/s
v = superficial velocity, m/s
x = axial coordinate, m
z = moving coordinate, Eq. 22, m

Greek letters

γ = constant, Eq. 33
Γ = surface concentration, mol/m^2
Γ_∞ = saturation adsorption, mol/m^2
σ = interfacial tension, N/m
ϕ = porosity
ψ_0 = interfacial potential, V

Subscripts/superscripts

o = oil
s = sublayer
w = water

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