Transient Ion Exchange and Solubilization of Limestone in an Oil Field Sandstone: Experimental and Theoretical Wavefront Analysis

The competition between calcium-sodium ion exchange and the solubilization of calcium carbonate is studied in a column packed with a sandstone from an oil field. An equilibrium model accounting for this coupling is described. It is shown that the preflush used to eliminate the exchangeable calcium has only a transient efficiency and that the salinity of the water after the preflush can no longer be decreased to a very low level when the solubilization process occurs.

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SCOPE

The use of anionic surfactants in enhanced oil recovery (EOR) processes involves many physicochemical processes: phase behavior (Bourrel et al., 1982); retention of the surfactant (Defives and Bazin, 1982; Novosad, 1981; Trogus et al., 1977; Fidgore, 1982; Somasundaran and Hanna, 1977; Sardin, 1984); precipitation and redissolution of the surfactant (Celik et al., 1979, 1982; Schweich, 1984); and the cation exchange process (Pope et al., 1978; Hirasaki, 1980, 1982; Griffith, 1978; Smith, 1978). In all of these processes the contact between the surfactant and calcium cations is of crucial importance. To avoid this contact a preflood with a sodium solution is used to eliminate the major part of the exchangeable calcium. In all the studies devoted to this process the only source of calcium cations is supposed to be the ion exchange with sodium on the clays. However, most sandstones in which the EOR process with surfactants is possible contain at least small amounts of calcium carbonate which dissolves in the aqueous phase and behaves as a uniformly distributed source of calcium ions. In this case the ion exchange process competes with the solubilization process and the exchange with sodium can never reach completion. At the same time, salinity with respect to calcium can no longer decrease down to a very low level (Bourdarot et al., 1984).

This problem is presently encountered in the French EOR pilot plant located in the oil field of Chateaurenard. This field consists of a residual oil phase trapped in a sandstone. The compositions of the sandstone and of the low concentrated brine are given in Table 1. It is seen that the sandstone contains 1% w/w of calcium carbonate. This is the reason we have investigated the competition between the solubilization of calcium carbonate and the ion exchange processes on this material.

CONCLUSIONS AND SIGNIFICANCE

The competition between transient calcium-sodium ion exchange and the simultaneous solubilization of calcium carbonate which occurs in a column packed with a sandstone from an oil field is presented. At steady state when the column is fed with demineralized water, the constant concentration (0.3 meq/L) of calcium found in the effluent is due to the calcium carbonate dissolved from the sandstone. In the transient state the responses to saturation fronts of sodium chloride (more than 1 meq/L) are very similar to those obtained in classical ion-exchange experiments and the solubilization process is only secondary. However, the situation is drastically different for desaturation fronts such as those that occur at the end of a sodium preflush. When the column is equilibrated with the sodium solution and then desaturated with demineralized water there is a transient decrease in the concentration of calcium from 0.3 meq/L down to 0.01 or 0.001 meq/L. This relative absence of calcium is observed to occur together with a plateau zone of sodium (several meq/L depending on the previous saturation). After this transient state the clays are again saturated with calcium due to the limestone which acts as a distributed source of calcium inside the column. It is shown that the plateau zone, which does not appear when solubilization is ignored, is due to the sodic clays acting as a water softener. They exchange their sodium and thus reduce the concentration of calcium due to the solubilization process as long as sodium is available on them. It is concluded that when the desaturation is considered as the end of a sodium preflush it has only a transient efficiency for eliminating the exchangeable calcium. An equilibrium model is derived to describe this transient coupling and to investigate the effect of the various parameters of the processes.

It is found that the plateau zone has the following properties:

1. The more concentrated the previous saturation with sodium, the less concentrated with respect to calcium and the shorter the plateau zone.

2. The concentrations in the plateau zone are independent of the exchange parameters and depend only on the solubility parameters of calcium carbonate and especially on the solubility product.

3. The length of the plateau zone depends on the selectivity factor of the ion exchange process and it is proportional to the exchange capacity.

4. In the plateau zone the pH may be as high as 10 or 11.

The model together with the experiments suggests that the solubilization process is a rate-limiting step in the plateau zone even for flow velocities as low as 0.02 m/day. This point seems to deserve further study.

INTRODUCTION:

Figure 1 illustrates the problem under study. A column is packed with the standstone from Chateaurenard and equilibrated with a flow of demineralized water. At steady state calcium is detected in the effluent. The injection of a slug (1.5 pore volume) of 20 meq/L of sodium chloride shows two phenomena:

1. A simple ion exchange process illustrated by the peak of calcium.
2. A plateau-zone of sodium is observed after the peak of calcium.

In this zone calcium has a very low concentration even though solubilization occurs. Moreover, all of the sodium injected is recovered although ion exchange with calcium has occurred. This is the illustration of the competition between the exchange and the solubilization process which proceeds as follows. In the slug, sodium progressively saturates the exchanging sites of the clays; behind the slug, demineralized water dissolves calcium carbonate and the clays act as a water softener; as soon as calcium is dissolved it is exchanged with sodium, and this process occurs as long as sodium remains on the clays. When the exchange is complete the whole amount of sodium is recovered, the clays are resaturated with calcium, and the background concentration of calcium due to the solubilization is found again.

The physicochemical information available on oil fields is generally rather poor. This means that sophisticated models accounting for as many processes as possible are generally useless and hide the most important processes responsible for the experimental results. Consequently we shall derive an equilibrium model which is known to give the main qualitative properties of the phenomena under study and some quantitative but approximate results. Finally we will discuss nonequilibrated processes.

EQUILIBRIUM CHEMISTRY OF ION EXCHANGE ACCOMPANIED BY LIMESTONE SOLUBILIZATION

The solutions are assumed to be ideal; the concentration of each species is described by its chemical symbol. The solubilization process deserves special attention in a gas-free porous medium. It is controlled by the solubility product of calcium carbonate and the ionization constants of carbonic acid and water:

$$P = Ca \cdot CO_3 \tag{1}$$

$$K_1 = H \cdot HCO_3/H_2CO_3 \tag{2}$$

$$K_2 = H \cdot CO_3/HCO_3 \tag{3}$$

$$K_e = H \cdot OH \tag{4}$$

When the partial pressure of carbon dioxide is given, the electroneutrality condition allows the composition of the solution in contact with the atmosphere to be calculated. In an oil field or a laboratory column the situation is different. While the feedstock solution is in equilibrium with the atmospheric carbon dioxide, it is not in equilibrium with calcium carbonate prior to the injection. When the solution enters the bed of sandstone, it equilibrates with calcium carbonate while further equilibration with atmosphere is prevented. This particular equilibration process leads to another composition of the solution especially with respect to pH. Let us consider a feedstock which contains calcium and sodium chloride and carbonic acid. Let:

$$z = H_2CO_3 + HCO_3 + CO_3 \tag{5}$$

be the total carbonate concentration and Ca* the concentration of calcium in the feedstock. Due to the electroneutrality condition we have:

$$Ca^* = (Cl - Na)/2 \tag{6}$$

When the solution equilibrates with the calcium carbonate with no gaseous phase, and equal excess of calcium and carbonate results:

$$Ca - Ca^* = H_2CO_3 + HCO_3 + CO_3 - z = Ca - (Cl - Na)/2 \tag{7}$$

TABLE 1. COMPOSITION OF SANDSTONE AND BRINE

Sandstone, % w/w		Brine, mg/L	
Quartz	95	Ca	64.0
Clays (Kaolinite 90%, Illite + Smectite 10%)	3	Mg	19.0
Calcite	1	Na	33.0
Feldspar, Siderite	Traces	K	8.5
		HCO_3	347.0
		Cl	27.0

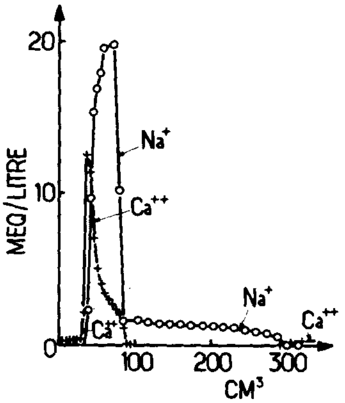

Figure 1. Calcium and sodium responses to injection of 1.5 pore volume of a 20 meq/L NaCl solution in a column previously equilibrated with demineralized water. The plateau zone following the peak of exchanged calcium shows the sodium released by the calcium due to the solubilization process.

TABLE 2. CONSTANTS, SOLUBILITY DATA, AND SOLUTION COMPOSITION

Equilib. Constants Used in Model mol/L		Solubility Products, P, in Literature Temp. °C	Value mol/L	Ref.
K_1	4.13×10^{-7}	20	3.2×10^{-9}	Olive (1978)
K_e	6.62×10^{-15}	25	4.3×10^{-9}	Al-Droubi et al. (1978)
K_2	4.19×10^{-11}	20	5.2×10^{-9}	Legrand et al. (1981)
P	7.19×10^{-9}			
z^*	1.2×10^{-5}			

Solution Composition, Ca CO_3 Solubility in Demineralized H_2O

	Atmosphere Equilibration With mol/L	Without mol/L
pH	8.38	10.06
H_2CO_3	1.2×10^{-5}	2.2×10^{-8}
CO_3	1.2×10^{-5}	5.1×10^{-5}
Ca	6.1×10^{-4}	1.4×10^{-4}
HCO_3	1.2×10^{-3}	1.05×10^{-4}
Ca (Experimental)	1.4×10^{-4}	

* z = amount H_2CO_3 dissolved in water.

When the composition of the feedstock is given (Na, Cl, and z) Eqs. 1–4, and 7 and the electroneutrality equation, Eq. 8, allow the composition of the solution to be calculated.

$$\mathrm{H + Na + 2Ca = OH + Cl + HCO_3 + 2CO_3} \tag{8}$$

Table 2 summarizes the equilibrium constants. The solubility product of calcium carbonate has been chosen to account for the observed experimental solubility in demineralized water. Our value is slightly higher than those used by Legrand et al. (1981), Olive (1978), Al-Droubi et al. (1978) listed in Table 2, however it is within the range of the values for impure calcium carbonate. The compositions of the solutions with and without equilibration with the atmosphere during the solubilization are also compared. It is seen that the absence of atmosphere decreases the solubility and increases the pH with respect to the other case. These results are in good agreement with those of Al-Droubi et al. (1978) and Garrels and Christ (1965). Although demineralized water has a pH of about 5.5, the special equilibration process involved raises the pH to 10. It means that H^+ concentration may be very low and in any case far lower than calcium concentration. This suggests that Ca^{++}/H^+ exchange will be meaningless and that Ca^{++}/Na^+ is the main exchange process.

The ion exchange process has been extensively studied (Hirasaki, 1980, 1982; Pope et al., 1978; Griffith, 1978; Smith, 1978; Helfferich and Klein, 1970). It will be described by a constant exchange capacity and a constant selectivity factor, K. As discussed above only calcium/sodium exchange will be considered:

$$K = \frac{\mathrm{Na}^2 \cdot \overline{\mathrm{Ca}}}{\overline{\mathrm{Na}}^2 \cdot \mathrm{Ca}} \tag{9}$$

$$\overline{N_E} = \overline{\mathrm{Na}} + \overline{2\mathrm{Ca}} \tag{10}$$

THEORETICAL MODEL FOR TRANSIENT WAVEFRONTS

The model is based on the classical assumptions of the so-called equilibrium models (Helfferich and Klein, 1970; Pope et al., 1978; Hirasaki 1982; Walsh et al., 1984).

1. The flow is one-dimensional. Dispersion, capillarity, gravity, and compressibility effects are neglected.
2. The isothermal phases are in local equilibrium everywhere.
3. Initial compositions of both phases are uniform.
4. The solutions (fluid and solid) are ideal.
5. The ion exchange process involves Ca^{++} and Na^+. It is described by a constant selectivity factor and a constant exchange capacity.
6. The flow never dissolves all of the calcium carbonate.
7. The feedstock consists of any mixture of $CaCl_2$ and NaCl in demineralized water. It is equilibrated with atmospheric carbon dioxide but not with calcium carbonate. As soon as the solution reaches the sandstone, it equilibrates with calcium carbonate with no further reequilibration with atmospheric carbon dioxide.

These assumptions will be discussed later. Equations 1–4 and 8–10 are the equilibrium relationships between the ten unknown concentrations: $\overline{\mathrm{Na}}$, $\overline{\mathrm{Ca}}$, H, OH, Cl, H_2CO_3, HCO_3, CO_3, Na, and Ca. Consequently three mass-balance equations are required. Two of them are:

$$u\frac{\partial \mathrm{Cl}}{\partial x} + \frac{\partial \mathrm{Cl}}{\partial t} = 0 \tag{11}$$

$$u\frac{\partial \mathrm{Na}}{\partial x} + \frac{\partial \mathrm{Na}}{\partial t} + \frac{M}{V_0}\frac{\partial \overline{\mathrm{Na}}}{\partial t} = 0 \tag{12}$$

The third equation is a stoichiometric invariant:

$$\begin{aligned} &F = \mathrm{Na + 2Ca\text{-}Cl\text{-}2(H_2CO_3 + HCO_3 + CO_3)} \\ &u\frac{\partial F}{\partial x} + \frac{\partial F}{\partial t} = 0 \end{aligned} \tag{13}$$

The derivation of Eq. 13 is given in the appendix and is based on the stoichiometric relationships between each species. Equation 7 is the boundary condition at the inlet of the system. From Eq. 13 it is seen that:

$$F(x = o,t) = -2z \tag{14}$$

Since Eq. 14 is a constant boundary condition for the mass-balance, Eq. 13, we have:

$$F(x,t) = 2z = \mathrm{2Ca + Na\text{-}Cl\text{-}2(H_2CO_3 + HCO_3 + CO_3)} \tag{15}$$

whatever x and t. Consequently the model consists of the algebraic equations 1–4, 8–10, and 15, and two partial differential equations, 11 and 12. It is solved either with the coherence principle (Helfferich and Klein, 1970) or the theory of hyperbolic systems of partial differential equations. We shall use the second approach without detail on its basis (see a brief outline in Schweich et al.,

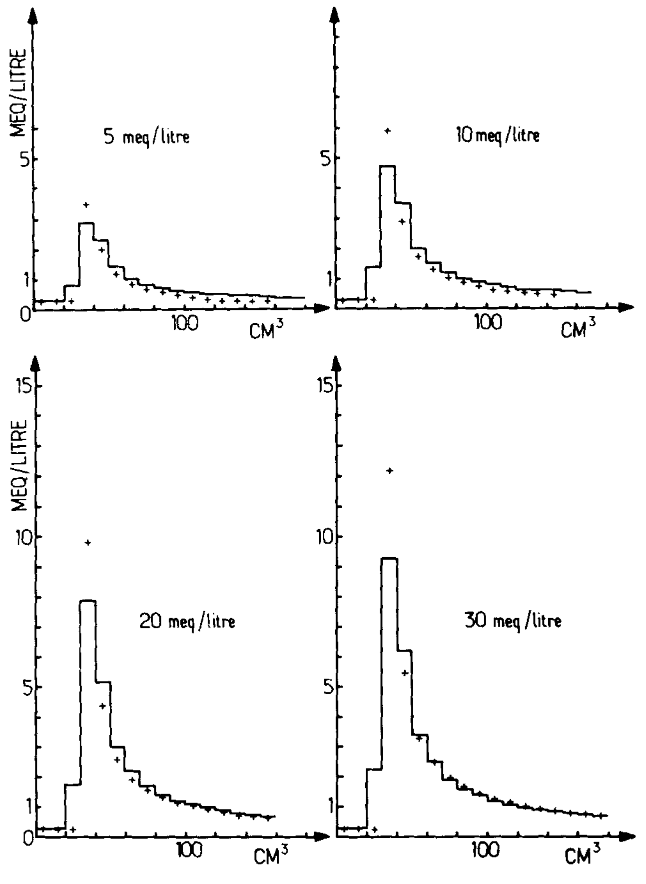

Figure 2. Elution curves of calcium due to various saturation fronts of NaCl. — experimental data; + model. The curves show the average concentrations in successive 10 cm³ fractions. Volumetric flow rate 2 cm³/min; pore volume 32 cm³.

1980). Na and Cl are chosen as the two independent concentrations which define a composition at a given time and position in the column. Then defining σ as the characteristic velocity of a composition, Eqs. 11 and 12 reduce to:

$$\begin{cases}(u-\sigma)d\mathrm{Cl} = 0\\ (u-\sigma)d\mathrm{Na} - \sigma\dfrac{M}{V_0}d\overline{\mathrm{Na}} = \left[u - \sigma\left\{1+\dfrac{M}{V_0}\left(\dfrac{\partial\overline{\mathrm{Na}}}{\partial\mathrm{Na}}\right)_{\mathrm{Cl}}\right\}\right]d\mathrm{Na}\\ \qquad\qquad - \sigma\dfrac{M}{V_0}\left(\dfrac{\partial\overline{\mathrm{Na}}}{\partial\mathrm{Cl}}\right)_{\mathrm{Na}}d\mathrm{Cl} = 0\end{cases} \tag{16}$$

σ is given by the nontrivial solutions of the system in Eqs. 16 when its determinant vanishes:

$$(u-\sigma)\left[u - \sigma\left\{1+\frac{M}{V_0}\left(\frac{\partial\overline{\mathrm{Na}}}{\partial\mathrm{Na}}\right)_{\mathrm{Cl}}\right\}\right] = 0 \tag{17}$$

Equation 17 shows that the elution curves due to a step composition change are composed of:

1. A sharp, but not self-sharpening, front which propagates with the constant velocity $\sigma = u$. This is a normality wave associated with the unretained chloride. In this first wave Eq. 16 reduces to $d\overline{\mathrm{Na}} = 0$, which means that the composition of the exchanger remains undisturbed as it does across a classical normality wave. Since the selectivity coefficient is assumed to be constant, Eq. 9 and the constant composition of the exchanger imply that across this first wave:

$$\mathrm{Na}^2/\mathrm{Ca} = \text{constant} \tag{18}$$

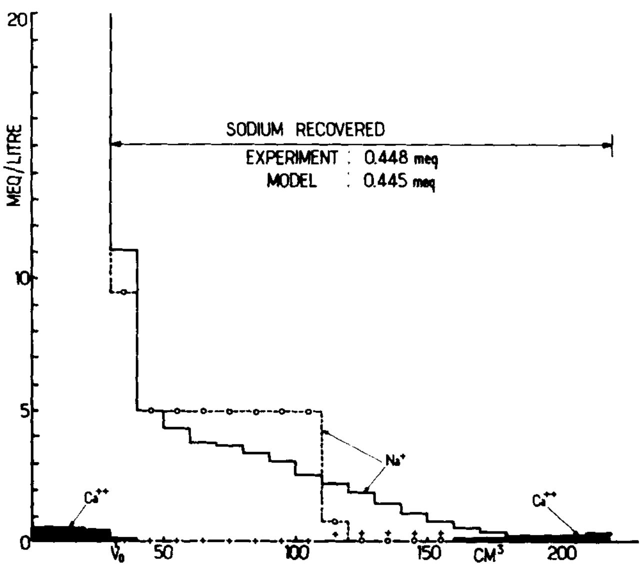

Figure 3. Desaturation with demineralized water of a column previously equilibrated with a 30 meq/L solution of NaCl; other conditions identical to Fig. 2. — experimental data; +, O model.

The value of this ratio is given by the downstream composition which is the initial state of the column.

2. A self-broadening wave which propagates with the velocity:

$$\sigma = u\Big/\left[1+\frac{M}{V_0}\left(\frac{\partial\overline{\mathrm{Na}}}{\partial\mathrm{Na}}\right)_{\mathrm{Cl}}\right] \tag{19}$$

Along this second wave, Eqs. 16 and 18 show that the chloride concentration is constant and given by the upstream composition. Although Eq. 18 looks like those derived for ion exchange alone (Helfferich and Klein, 1970), the solubilization parameters are involved in the derivative $(\partial\overline{\mathrm{Na}}/\partial\mathrm{Na})_{\mathrm{Cl}}$. The complete set of equations allowing $(\partial\overline{\mathrm{Na}}/\partial\mathrm{Na})_{\mathrm{Cl}}$, σ, Na, Cl and Ca to be calculated is given in the appendix. When a purely self-sharpening front occurs Eq. 19 must be replaced by:

$$\sigma = u\Big/\left[1+\frac{M}{V_0}\frac{\Delta\overline{\mathrm{Na}}}{\Delta\mathrm{Na}}\right] \tag{20}$$

in which $\Delta\mathrm{Na}$ and $\Delta\overline{\mathrm{Na}}$ are the jumps in the concentrations. We shall see that no further mathematical refinements are necessary though combined waves (partly self-broadening, partly self-sharpening) may occur. Finally the elution volume of a given composition is given by $V = V_0u/\sigma$.

COMPARISON BETWEEN THEORY AND EXPERIMENTS

The column is packed with 115 g of sandstone which has been previously washed with dioxan to remove as much as possible any trace of residual oil. The porous medium is then saturated with an upward flow of water (0.2 cm³/min). Residence time distribution measurements showed that the pore volume was 32 cm³ and that the Peclet number was 200 for a bed height of 14.7 cm. The experiments were performed at room temperature and the effluent was sampled with a fraction collector. These fractions were analyzed by atomic adsorption spectrometry, which gives the discontinuous concentration curves of Figures 2 and 3.

Figure 2 shows calcium eluted for various saturation fronts when the column is fed with sodium chloride. The clays were previously saturated with calcium and then equilibrated with demineralized

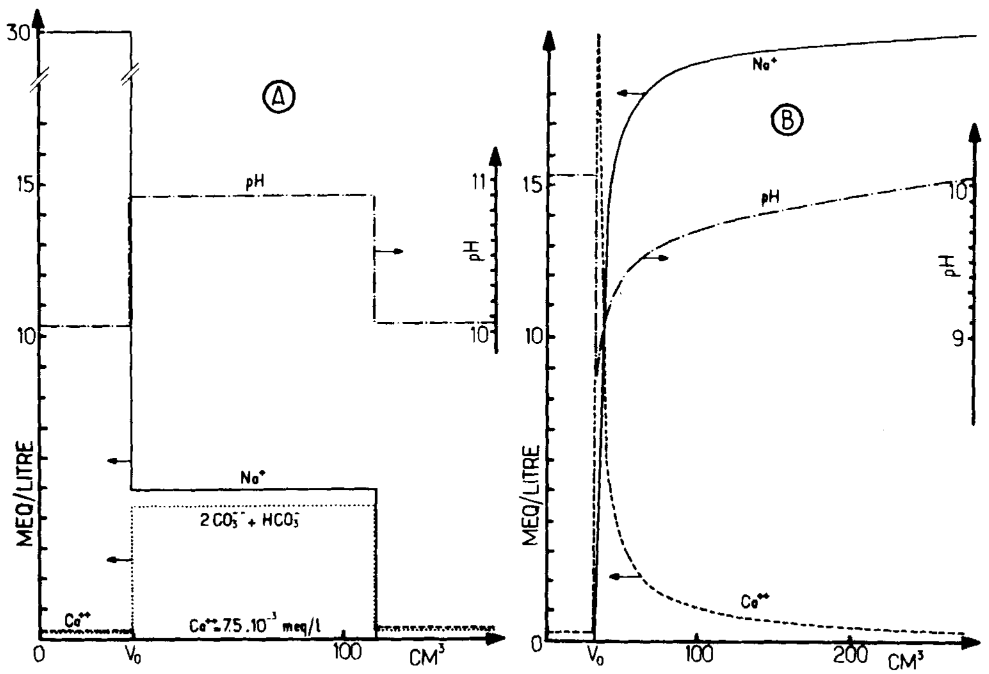

Figure 4. Theoretical responses without the averaging due to fraction collection. A: 30 meq/Liter desaturation front as in Fig. 3. B: 20 meq/L saturation front of NaCl as in Fig. 2. Parameters: standard values of Table 2 and Eq. 21.

water. The points marked as crosses are the average concentration in each fraction obtained from the equilibrium model described above with the following exchange parameters:

$$K = 1{,}100\ \mathrm{kg/L}$$

$$\overline{N}_E = 7.4 \cdot 10^{-3}\ \mathrm{eq/kg} \qquad (21)$$

It is seen that the agreement is good except at the peak maximum. This is mainly due to the dispersion process, which is neglected in the model. An important feature of these experiments is that the amount of calcium recovered is not a measure of the exchange capacity. This amount increases with the sodium concentration of the saturation front. This is due to the low concentration of calcium due to the solubilization process, which prevents a complete exchange when steady state is reached. Some identical experiments were performed with a lower volumetric flow rate and gave identical results, showing that equilibrium is reached in these experiments.

Figure 3 shows the desaturation with demineralized water of a column equilibrated with a 30 meq/L solution of sodium chloride. The transient lack of calcium is still observed (see Figure 1) but the plateau zone of sodium is now a tail spread over six pore volumes. Conversely, the model predicts that the second wave is self-sharpening. If the concentration of calcium is predicted well by the model, it can be seen that the agreement is very poor for the sodium plateau zone. However the second sharp boundary is accurately located in the middle of the sodium tail. The discrepancy observed in Figure 3 will be discussed in the following section.

DISCUSSION

The good agreement and also the poor agreement observed in Figures 2 and 3 are intimately connected with the very nature of the coupling between Na^+/Ca^{++} ion exchange and calcium carbonate solubilization. We shall first deal with the physical explanation responsible for the predicted plateau zone when a desaturation experiment is performed.

Upstream of the normality wave the calcium cations generated by the solubilization process are exchanged with the sodium of the clays, which explains the decrease of the calcium concentration. However the carbonate ions which are generated by the solubilization process accumulate in the solution and their concentration increases until it balances the concentration of calcium according to the solubility product. This is why the sodium is not instantaneously released. Moreover it means that in the plateau zone the charge of sodium ions is balanced by carbonate ions and therefore the pH must be high. Figure 4A shows the predicted fronts of Ca, Na, pH and the normality of total carbonate ions ($2CO_3 + HCO_3$). The difference between the curves of total carbonate and sodium is due to the OH^- anions. In the experiment the pH was found one unit lower than that predicted by the model. However it should be noticed that the pH measurement is not accurate in this solution of low ionic strength. Moreover, our model based on the assumption of ideal solutions predicts a pH which is slightly too high. Unfortunately it was impossible to analyze the effluent for the carbonate ions since the equilibration of any sample with a gaseous phase would give falsified results.

In the saturation experiments illustrated in Figure 2, the solubilization process becomes secondary. As soon as calcium is exchanged its concentration becomes so high that it stops the solubilization according to the solubility product. The competition is significant only when low-concentration saturation fronts are performed (less than 1 meq/L). Figure 4B shows typical sodium, calcium, pH, and carbonate normality curves. As soon as solubilization is stopped by the exchanged calcium, the pH decreases but it remains greater than the pH of the feedstock (pH 5.5).

From the above remarks it may be concluded that a saturation front of sodium inhibits the solubilization process which, on the other hand, is favored by a desaturation with pure water. This immediately explains why the experiments of Figure 2 are not limited by the mass-transfer kinetics of the solubilization process. Conversely in the plateau zone of Figure 3 or 1 the exchange process is a sink for calcium ions and the solubilization process may become the rate-limiting step and may explain the poor agreement between the model and the experiment. This is supported by

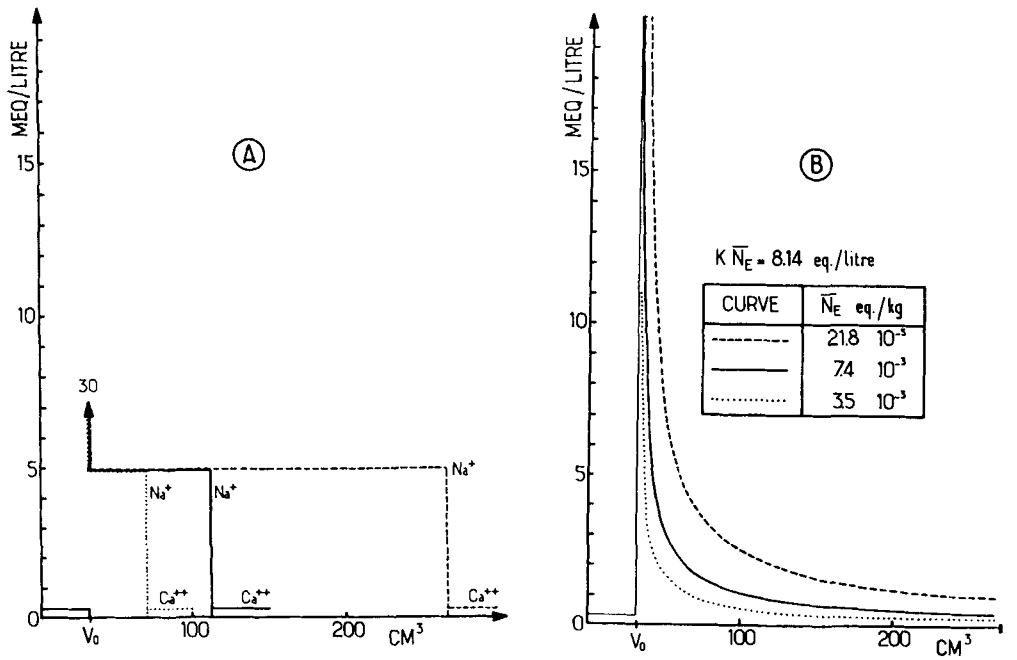

Figure 5. Effect of clay content or exchange capacity on Ca and Na; conditions as in Fig. 4 except for *K* and $\bar{N}_E$. Curves in B show only Ca; — standard case of Fig. 4.

similar experiments performed with a lower flow rate (0.008 cm^3/min) which show that the concentration of sodium increases slightly in the plateau zone while its duration decreases slightly. However our experimental results do not allow us to determine the flow velocity which is required for the solubilization process to reach equilibrium in the plateau zone. We can only assert that it is less than 2.3 × 10^{-2} m/d. This being a very low value for an oil field, we think that the rate of the solubilization process may always be the rate-limiting step in the phenomena induced by a desaturation front.

Although the equilibrium model cannot account accurately for the experimental results, it has been used to investigate the qualitative behavior of the system and especially the sensitivity to various parameters and the coherence of the assumptions. The most questionable assumption concerns the absence of exchange process with H$^+$ ions which could be involved in the desaturation experi-

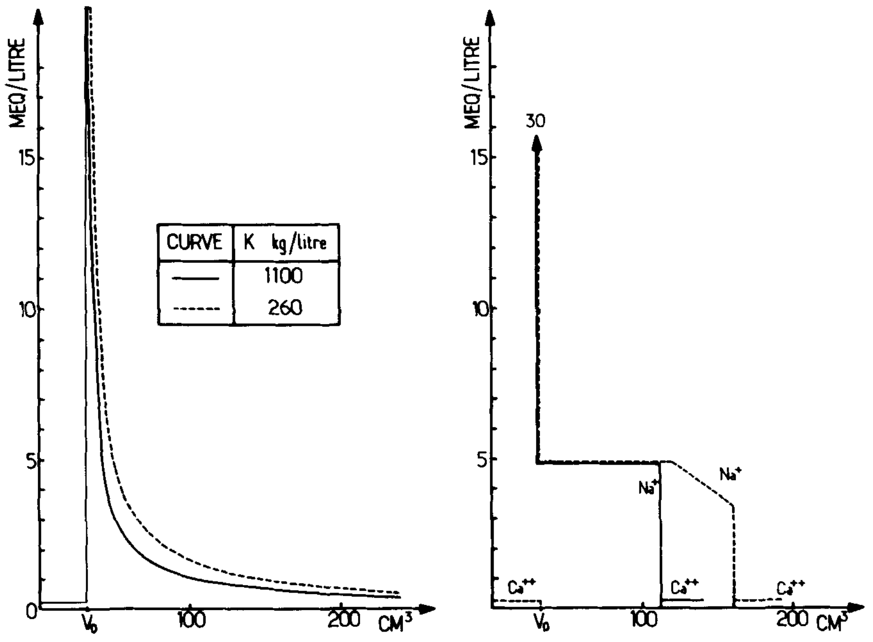

Figure 6. Effect of the selectivity factor; conditions as in Fig. 4 except for *K*. Note combined front at the end of the plateau zone for the lower *K*. Curves in B show only Ca; — standard case of Fig. 4.

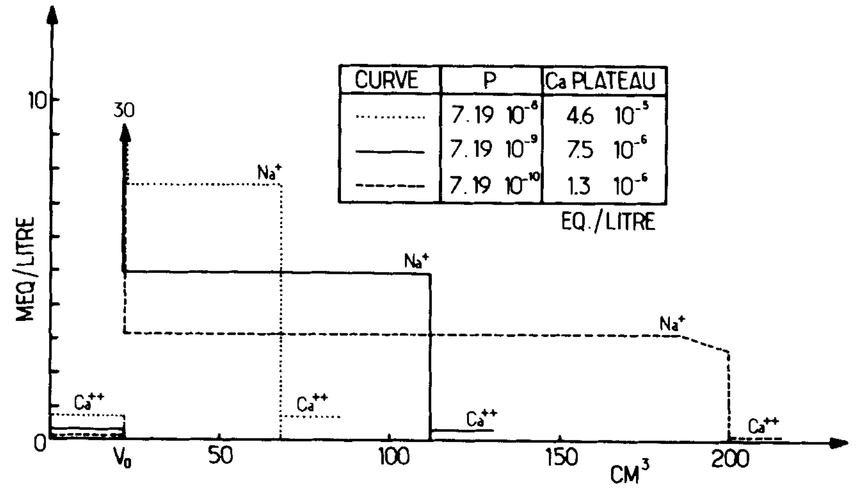

Figure 7. Effect of solubility product of calcium carbonate on the plateau zone; conditions as in Fig. 4A except for the solubility product *P*. — standard case of Fig. 4.

ments when no exchangeable cations are injected. However it is found experimentally (Figure 3) and theoretically (Figure 4) that calcium is at least 10^5 times more concentrated than H^+. It is thus concluded that the exchange with H^+ is meaningless since the values of the selectivity factors for the H^+/Na^+ exchange are commonly found to be about 10 (Wahlberg et al., 1965).

The sensitivity of the response curves to the amount of clays in the sandstone is illustrated in Figure 5, and Figure 6 shows the effect of the selectivity factor. In these two figures the chosen values of $\overline{N}_E$ and K are within the range of the most common values found in the literature dealing with sandstone. In Figure 5, $\overline{N}_E$ accounts for the clay content. For each curve the product $K\overline{N}_E$ is kept constant to account for a given affinity of the clays for calcium. In the case of saturation fronts the amount and the concentration of calcium recovered increases with the exchange capacity as expected. For desaturation fronts, the concentration in the plateau zone is constant according to the properties of the first wavefront given by Eq. 18. However the duration of the plateau is proportional to the exchange capacity. In Figure 6 the effect of the selectivity factor is more complex. When it decreases, the peak of calcium due to a saturation front has a longer tail, which seems to contradict the classical results of ion-exchange models. In fact it is the dissolved calcium carbonate which increases the concentration in the tail. For desaturation fronts the plateau zone has always the same composition (Eq. 18) but its duration increases. This is due to a greater extent of saturation with sodium for low values of the selectivity coefficient.

Finally, Figure 7 shows the effect of the solubility product of calcium carbonate, which may vary greatly according to the crystalline structure of the solid and the amount of impurity, especially magnesium. For saturation fronts the effect is very slight and only the very ends of the calcium peak are affected. For desaturation fronts the amount of sodium recovered is constant, however its concentration in the plateau zone decreases with the solubility product, which governs the ratio implied in Eq. 18. Conversely, the length of the plateau zone increases as the solubility product decreases. The curves illustrate extreme situations for very low and very high solubility of impure calcite.

In any case, the desaturation fronts considered as the end a preflush show that a transient high decrease of the concentration of calcium can be achieved. However the salinity of the water cannot be reduced very much due to the plateau-zone of sodium. Conversely for saturation fronts the elution of calcium behaves as in classical ion exchange and the solubilization process is only secondary. The effect of these saturation fronts on the transient flow of a slug of low concentrated anionic surfactant has been studied by Sardin (1984) and Schweich (1984). They have shown that according to the calcium concentration either the partitioning of the surfactant with the oil phase or the precipitation is favored. The present paper shows how to monitor this calcium concentration to favor the partition process which is responsible for the efficiency of the recovery process (Bourdarot et al., 1984).

It seems to us that future research on this problem should be devoted to the kinetics of the solubilization process. Confirmation that this is the rate-limiting step would be very useful since the slower the solubilization rate, the smaller the concentrations in the plateau zone and the longer its duration. Conversely, the study of the behavior of sodium bicarbonate injections should give meaningful data, since the injected carbonate ions would inhibit the solubilization process. Future papers will be devoted to these problems.

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NOTATION

Ca,Na = fluid phase concentrations of species denoted by chemical symbols, mol/L^{-1}
$\overline{Ca},\overline{Na}$ = solid phase concentrations, mol/kg^{-1}
F = defined by Eq. 13
G = defined by Eq. A12
K = selectivity factor, kg/L^{-1}
K_1,K_2 = ionization constants of carbonic acid
K_e = ionization constant of water
$\underline{M}$ = mass of sandstone, kg
$\overline{N}_E$ = exchange capacity, eq/kg^{-1}
P = solubility product
r = rate of reaction (see appendix)
t = time, s
u = linear flow velocity, m/s^{-1}
V,V_0 = elution volume, pore volume, cm^3

x = abscissa, m
z = total carbon content of feedstocks, mol/L^{-1}

Greek Letters

σ = velocity of a composition

APPENDIX

Calculation of $(\partial \overline{\mathrm{Na}}/\partial \mathrm{Na})_{\mathrm{Cl}}$

Let N_o be the total normality with respect to sodium and calcium:

$$N_o = \mathrm{Na} + 2\mathrm{Ca} \tag{A1}$$

The selectivity factor is:

$$K = \frac{\mathrm{Na}^2}{\overline{\mathrm{Na}}^2} \frac{\overline{N_E} - \overline{\mathrm{Na}}}{N_o - \mathrm{Na}} \tag{A2}$$

Solving Eq. A2 for $\overline{\mathrm{Na}}$ gives:

$$\overline{\mathrm{Na}} = \frac{\mathrm{Na}^2}{2K(N_o - \mathrm{Na})} [\sqrt{A} - 1], \quad A = 1 + 4K \frac{\overline{N_E}}{\mathrm{Na}^2} (N_o - \mathrm{Na}) \tag{A3}$$

Then:

$$\left(\frac{\partial \overline{\mathrm{Na}}}{\partial \mathrm{Na}}\right)_{\mathrm{Cl}} = \left(\frac{\partial \overline{\mathrm{Na}}}{\partial \mathrm{Na}}\right)_{\mathrm{Cl},N_o} + \left(\frac{\partial \overline{\mathrm{Na}}}{\partial N_o}\right)_{\mathrm{Na,Cl}} \cdot \left(\frac{\partial N_o}{\partial \mathrm{Na}}\right)_{\mathrm{Cl}} \tag{A4}$$

From Eq. A3 we have:

$$\begin{aligned}\left(\frac{\partial \overline{\mathrm{Na}}}{\partial \mathrm{Na}}\right)_{\mathrm{Cl},N_o} &= \left(1 - 2\frac{N_o}{\mathrm{Na}}\right)\left(\frac{\partial \overline{\mathrm{Na}}}{\partial N_o}\right)_{\mathrm{Na,Cl}} \\ &= \mathrm{Na}^2\left(1 - 2\frac{N_o}{\mathrm{Na}}\right)\left[\frac{\sqrt{A} - 1}{2K(N_o - \mathrm{Na})^2} \right. \\ &\quad \left. - \frac{\overline{N_E}}{\sqrt{A}\,\mathrm{Na}^2(N_o - \mathrm{Na})}\right]\end{aligned} \tag{A5}$$

Equation A5 allows to write Eq. A4 as:

$$\left(\frac{\partial \overline{\mathrm{Na}}}{\partial \mathrm{Na}}\right)_{\mathrm{Cl}} = \left[\left(\frac{\partial N_o}{\partial \mathrm{Na}}\right)_{\mathrm{Cl}} + 1 - 2\frac{N_o}{\mathrm{Na}}\right]\left(\frac{\partial \overline{\mathrm{Na}}}{\partial N_o}\right)_{\mathrm{Na,Cl}} \tag{A6}$$

In the above equation only $(\partial N_o/\partial \mathrm{Na})_{\mathrm{Cl}}$ has to be eliminated. Let us find f such that:

$$d\,N_o = d\mathrm{Cl} + f\,d\mathrm{Ca} \tag{A7}$$

By use of the equilibrium relationships, Eqs. 1–5, 13, and their differential form, a straightforward but tedious calculation yields:

$$f = -\frac{2P}{\mathrm{Ca}^2}\frac{(1 + K_e/H^2)(1 + H/K_2 + H^2/K_1K_2) - (1 + 4H/K_1 + H^2/K_1K_2)P/K_2\mathrm{Ca}}{K_e/H^2 + 1 + (1 + 4H/K_1)P/K_2\mathrm{Ca}} \tag{A8}$$

Thus we have:

$$\left(\frac{\partial N_o}{\partial \mathrm{Ca}}\right)_{\mathrm{Cl}} = f \tag{A9}$$

From Eq. A1 we obtain:

$$\left(\frac{\partial N_o}{\partial \mathrm{Na}}\right)_{\mathrm{Cl}} = f\left(\frac{\partial \mathrm{Ca}}{\partial \mathrm{Na}}\right)_{\mathrm{Cl}} = \frac{f}{f - 2} \tag{A10}$$

When a fluid phase composition is computed from the algebraic equilibrium relationship, f is computed from Eq. A8, $(\partial N_o/\partial \mathrm{Na})_{\mathrm{Cl}}$ from Eq. A10, $(\partial \overline{\mathrm{Na}}/\partial N_o)_{\mathrm{Na,Cl}}$ from Eq. A5, and $(\partial \overline{\mathrm{Na}}/\partial \mathrm{Na})_{\mathrm{Cl}}$ from Eq. A6.

Derivation of Eq. 13

Let us consider the following reactions together with their kinetic rates:

$$\begin{matrix} H_2CO_2 \rightleftarrows HCO_3^- + H^+ & r_1 \\ HCO_3^- \rightleftarrows CO_3^= + H^+ & r_2 \\ H_2O \rightleftarrows OH^- + H^+ & r_3 \end{matrix} \tag{A11}$$

The pseudospecies of concentration:

$$G = 2H_2CO_3 + HCO_3 + H - OH \tag{A12}$$

is produced with the kinetic rate:

$$r_G = 2r_1 + (r_1 - r_2) + (r_1 + r_2 + r_3) - r_3 = 0 \tag{A13}$$

Thus we have:

$$u\frac{\partial G}{\partial x} + \frac{\partial G}{\partial t} = 0 \tag{A14}$$

Equation A14 is also valid when the equilibrium is reached in the stoichiometric relationships, Eq. A11.

With the electroneutrality equation, Eq. 8, we obtain:

$$\begin{aligned} G &= 2H_2CO_3 + HCO_3 + H\text{–}OH \\ &\qquad + OH + Cl + HCO_3 + 2CO_2\text{–}H\text{–}Na\text{–}2Ca) \\ G&: -[2Ca + Na\text{–}Cl\text{–}2(H_2CO_3 + HCO_3 + CO_3)] \\ G &= -F \end{aligned} \tag{A15}$$

Equation 13 is deduced from Eqs. A14 and A15.

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