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**DESIGN AND OPTIMIZATION OF PHOSPHATE-CONTAINING  
ALKALINE FLOODING FORMULATIONS**

Topical Report

By  
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# DESIGN AND OPTIMIZATION OF PHOSPHATE-CONTAINING ALKALINE FLOODING FORMULATIONS

by Troy R. French

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## ABSTRACT

Research conducted at NIPER has shown that the adverse reactions of strong alkalis can be reduced by using weaker alkaline agents. However, lower pH alkalis do not achieve the ultra-low IFT values necessary for significant mobilization of oil. It was discovered in 1985 that the addition of very small concentrations of synthetic surfactant to weakly alkaline solutions could significantly improve oil mobilization.

Alkaline agents can reduce losses of surfactant and permit the use of the low concentrations of surfactants used in surfactant-enhanced alkaline flooding. The weakly alkaline agents usually used are sodium carbonate, sodium bicarbonate, and sodium sesquicarbonate. Alkaline agents such as sodium carbonate remove many, but not all, of the divalent ions from reservoir brine. Additional means for preventing deleterious precipitation reactions that cause loss of anionic surfactants are desirable.

All phosphates, including orthophosphate, are highly charged and will associate with cations in solution. In addition to simple ion association, there is a tendency to form covalent bonds between phosphate groups and cations. Between pH 9.5 and 10.5, most of the phosphate ions exist in the form of monohydrogen phosphate, which readily forms complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{+2}$  cations. The complexation of calcium and magnesium ions by monohydrogen phosphate will further protect the low concentration of synthetic surfactant in surfactant-enhanced alkaline flooding, and at the same time provide an additional source of alkalinity. The effects of divalent ions on the IFT behavior of optimized formulations that include phosphate ions, and the effects of several parameters on surfactant adsorption and transport through porous media are the topics of this report.

The phase behavior and interfacial activity of mixtures containing sodium phosphate, sodium carbonate, sodium bicarbonate, surfactant, and crude oils were studied at three pH levels in order to identify combinations that produce interfacial activity. Three crude oils with total acid numbers (TAN) that range from very low to moderate were tested. Laboratory data are presented which show that alkali and synthetic surfactants produce interfacial properties that are more favorable for increased oil mobilization than either alkali or surfactant alone. Optimal salinities were found for producing the best interfacial activity with all three crude oils and the phosphate-containing surfactant-enhanced alkaline chemical system, and low levels of calcium ions had no detrimental effect on the IFT behavior.

Coreflood experiments were performed with an anionic surfactant that is designed for use in EOR applications. The corefloods were performed at pH 6.3 (natural pH of the system) and at pH 10.2 in oil-free Berea sandstone cores at ambient temperature (23° C) and at 52° C. The corefloods revealed that surfactant transport through porous media was improved by increasing temperature, pH, and permeability and by decreasing total ionic strength.

The coreflood results indicate that the transport of some surfactants through sandstone reservoirs that are heterogeneous in permeability and salinity may not correlate with fluid flow patterns. It was concluded that it is possible to transport low concentrations of surfactant (under alkaline conditions) through sandstone reservoirs when chemical formulations are properly designed.

## **BACKGROUND**

For well over a half century, it has been known that strong alkaline agents have the potential to increase oil recovery. Yet, field tests using strong alkaline chemical flooding formulations have always performed poorly. The poor performance of alkaline waterfloods has been shown to be due primarily to high consumption of alkaline chemicals within reservoirs.<sup>1</sup>

Since 1984, research conducted at NIPER has shown that the adverse reactions of strong alkalis can be reduced by using weaker alkaline agents. However, the lower pH alkalis do not achieve the ultra-low IFT values necessary for significant mobilization of oil. It was discovered in 1985 that the addition of very small concentrations of synthetic surfactant to weak alkaline solutions could significantly improve oil mobilization with weak alkaline chemicals.<sup>1,2</sup>

In addition to the synergism between alkali and surfactant that results in low IFT values, a surfactant-enhanced alkaline formulation provides another benefit. Since alkaline reagents reduce the adsorption of surfactants in reservoirs, low concentrations of surfactants can be used in field projects. The use of low concentrations of synthetic surfactants can markedly improve the economics of the process.

Weakly alkaline agents such as sodium carbonate, sodium bicarbonate, and sesquicarbonate are usually used. Monohydrogen phosphate ions have some desirable properties that may reduce loss of surfactant even more, and the use of weak alkaline mixtures that include monohydrogen phosphate ions is currently being investigated.

## INTRODUCTION

Alkaline agents provide protection from loss of low-concentration surfactants used in surfactant-enhanced alkaline flooding. Alkaline agents such as sodium carbonate remove many, but not all, of the divalent ions from reservoir brine. Additional means of protecting anionic surfactants from deleterious precipitation reactions with  $\text{Ca}^{2+}$  and  $\text{Mg}^{+2}$  are desirable. It has long been recognized that certain chemical agents can reduce the activity of divalent cations. Polyphosphates and organic chelating agents have been used for this purpose.<sup>3-4</sup>

It is also known that all phosphates, including orthophosphate, are highly charged and will associate with cations in solution. In addition to simple ion association, there is a tendency to form covalent bonds between phosphate groups and cations. The complexation that occurs is due to both ionic and covalent contributions to the overall bond. The amount of covalent character is lowest for sodium<sup>5</sup> and highest for transition elements such as iron.<sup>6</sup>

The equilibrium constants for monohydrogen phosphate ( $\text{HPO}_4^-$ ) complexes are given in the literature<sup>5</sup> and are reproduced in table 1. The calculated fraction of phosphate ions that exist as monohydrogen phosphate at various pH values are shown graphically in figure 1. Between pH 9.5 and 10.5, most of the phosphate ions exist in the form of monohydrogen phosphate, which readily complexes cations. The resultant complexing of calcium and magnesium ions by monohydrogen phosphate will further protect the low concentration of synthetic surfactant in surfactant-enhanced alkaline flooding, and, at the same time, provide an additional source of alkalinity. These pH values are also low enough to avoid the worst mineral-alkali reactions in an oil reservoir, while maintaining the ability to activate many organic acids.<sup>7</sup>

Another way alkaline agents protect the surfactant is by reducing adsorption of surfactant onto reservoir rock. Alkaline chemicals have been shown to reduce loss of surfactant by adsorption,<sup>3,4,8</sup> and there is no reason to believe that the addition of phosphates to alkali/surfactant formulations will diminish this effect.

TABLE 1. - Complex formation by phosphates

Equilibrium	Log eq. constant
$\text{Mg}^{++} + \text{HPO}_4^- = \text{MgHPO}_4 \text{ (aq)}$	2.5
$\text{Ca}^{++} + \text{HPO}_4^- = \text{CaHPO}_4 \text{ (aq)}$	2.7
$\text{Fe}^{3+} + \text{HPO}_4^- = \text{FeHPO}_4^+ \text{ (aq)}$	8.3

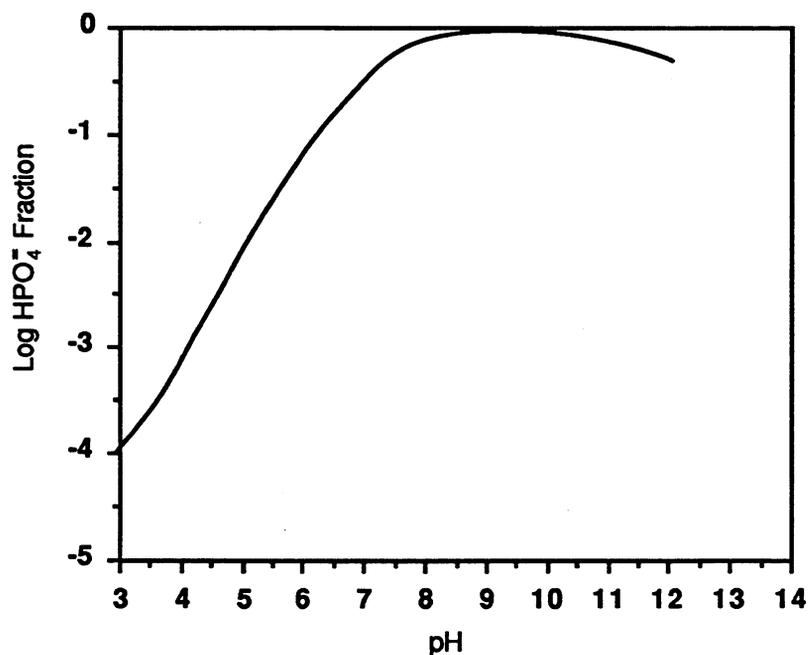


FIGURE 1. - Effect of pH on orthophosphate ( $\text{HPO}_4^-$ ) species fraction.

The effects of divalent ions on the IFT behavior of optimized formulations that include phosphate ions and the effects of several parameters on surfactant adsorption and transport through porous media are the topics of this report.

The research can be divided into three related areas:

1. The phase behavior of mixtures containing sodium phosphate, sodium carbonate, sodium bicarbonate, surfactant, and crude oils was studied at three pH levels in order to identify combinations that produce interfacial activity. Three crude oils with total acid numbers (TAN) that range from very low to moderate were tested to determine if a surfactant/carbonate/phosphate mixture is effective with crude oils that have very different TAN values.
2. Interfacial tension (IFT) studies were conducted with selected systems that exhibited favorable phase behavior. One crude oil with very low TAN and one with moderate TAN were selected for IFT measurements. The effect of divalent ions on transient IFT behavior was also studied because low levels of divalent ions remain in a reservoir even after an alkaline preflush.
3. Surfactant transport in oil-free Berea sandstone cores was monitored. The effects of permeability, temperature, salinity, pH and ionic strength were parameters of interest.

## ACKNOWLEDGMENTS

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## EXPERIMENTAL PROCEDURES

### Chemicals and Reagents

#### Crude oils

The crude oils were selected to represent a range of acid contents and API gravities. The crude oils were obtained from Kern River (CA), Wilmington (CA), and Delaware-Childers (OK) oil fields. The crude oil properties are summarized in table 2.

#### Surfactants

Two surfactants, one anionic and one nonionic, were used in the experiments. Petrostep B-100 is a commercial petroleum sulfonate produced by Stepan Company. It is designed for use in low-concentration surfactant flooding and is being used in at least one alkaline flooding field project.<sup>9</sup> Neodol 25-9 is a nonionic ethoxylated alcohol produced by Shell Chemical Company. It contains, on average, 9.2 ethylene oxide groups /mole.

#### Brines

The synthetic brines contained sodium chloride or sodium chloride and calcium chloride.

TABLE 2. - Crude oils

Oil	Gravity, ° API	Total acid number, mg/g KOH
Delaware-Childers	33.0	0.13
Wilmington	18.0	1.59
Kern River	11.9	2.36

### Alkaline Solutions

The alkaline solutions used for the experiments were prepared from sodium monohydrogen phosphate, sodium carbonate, and sodium bicarbonate. Approximate solution compositions were determined by titrating a mixture of sodium bicarbonate and sodium monohydrogen phosphate with sodium hydroxide. The compositions of the alkaline solutions used for the phase behavior tests are given in table 3. The pH values for the alkaline solutions are 9.5, 10.0, and 10.5.

### Interfacial Activity

#### Phase Behavior

Equal volumes (4-mL) of oil and aqueous phase were sealed in 10-mL graduated ampoules. The samples were placed in an oven at 52° C. Observations were made after 1 week. The samples were observed at that time and evaluated. The samples were then evaluated while being shaken. Finally, the samples were evaluated again after 1 more day. The observation while shaking provided information about the type of emulsion formed (oil-in-water or water-in-oil), the ease of emulsification, the stability of the emulsion (while shaking), and the amount (qualitative) of oil emulsified. The final evaluation (1 day after shaking) provides additional data on emulsion stability.

The emulsions formed were evaluated according to the following criteria:

<u>Emulsion quality</u>	<u>Criteria</u>
0	No visible emulsification
1	Black emulsion
2	Brown emulsion that changes to black while shaking
3	Brown emulsion
4	Brown emulsion containing >90% of the oil in the sample

Higher values of "emulsion quality" correlate with greater interfacial activity and nearness to optimal conditions. This visual method for determining optimal salinity for producing interfacially active systems is only slightly different from the visual methods that are used by others.<sup>10-11</sup>

TABLE 3. - Alkaline solutions

pH (25°C)	Na <sub>2</sub> HPO <sub>4</sub> (M)	Na <sub>2</sub> CO <sub>3</sub> (M)	NaHCO <sub>3</sub> (M)
9.5	0.065	0.0156	0.0494
10.0	0.065	0.0325	0.0325
10.5	0.065	0.0546	0.0104

## **Interfacial Tension**

Interfacial properties of selected systems were measured with a spinning drop interfacial tensiometer at 52° C. The transient IFT behavior was monitored over a time interval of several hours.

## **Surfactant Transport in Porous Media**

### **Coreflood procedure**

Unfired, oil-free Berea cores (25.4 X 3.7 cm) were mounted in Hasseler-type coreholders. Frontal advance rates were approximately 0.5 ft/d, providing a core residence time of about 1.7 days. The floods were conducted at two temperatures, 23° C (ambient) and 52° C (oven-controlled).

### **Analytical**

The analytical methods used for measurement of surfactant concentration were two-phase titration and HPLC. The two-phase titration was described by Rosen and Goldsmith<sup>12</sup> and the HPLC procedure is very similar to that described by Hofman and Angstadt.<sup>13</sup> The wavelength used for absorbance measurement of Petrostep B-100 surfactant was 222 nm (fig. 2) which is very close to the wavelength selected by Hofman and Angstadt.

## **RESULTS AND DISCUSSION**

### **Phase Behavior**

#### **Moderate TAN Oils**

Crude oil from Kern River (CA) oil field was tested at surfactant concentrations from 0.1 to 0.8 wt %, as shown in figures 3 through 5. The tests were conducted at 52° C with two surfactants. Each surfactant was tested at pH 9.5, 10.0 and 10.5. Each figure corresponds to one of the above pH levels. A figure is shown only if quality 3 or 4 emulsions, which correspond to high interfacial activity, were observed at that pH level. Thus, no figure is shown for surfactant B-100 at pH 9.5 because high interfacial activity was not observed at that pH.

In general, the phosphate-containing B-100 formulation exhibited interfacial activity with the Kern River oil at pH 10.0 and pH 10.5 and from 0.6 to 1.0% sodium chloride concentrations. The phase behavior was largely independent of surfactant concentration between 0.1 and 0.8% surfactant.

A photograph at 0.2% surfactant concentration is shown in figure 6. Several of the sample tubes in the photograph are difficult to interpret because oil from Kern River field wets the glass surfaces at some conditions. For example, the samples at 6% sodium chloride concentration have clear aqueous phases that are obscured by the oil-wet glass surfaces. It can, however, be easily observed in the photograph that at pH 10.5, the samples corresponding to 0.6 and 1.0% sodium chloride concentrations produced large quantities of brown oil-in-water emulsions. Previous results<sup>14</sup> have shown that emulsions of this type

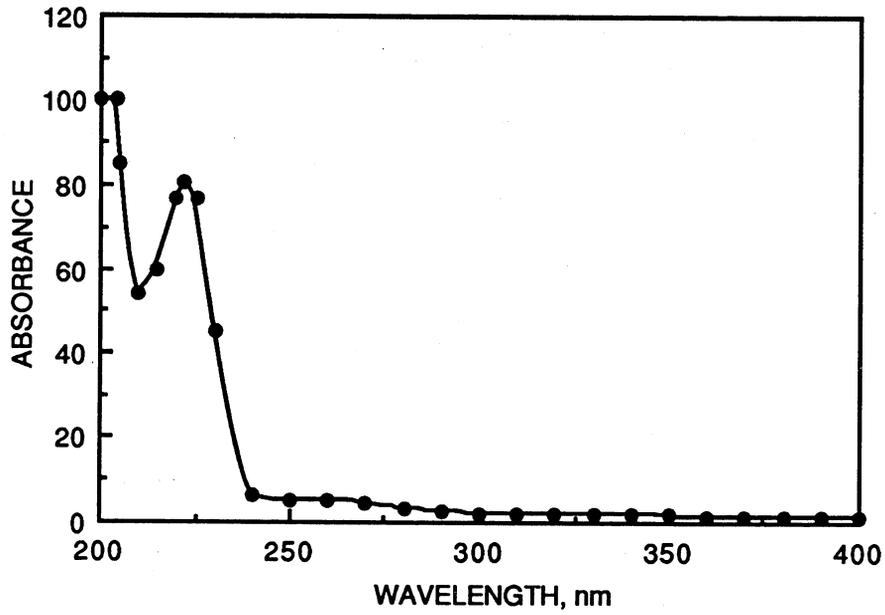


FIGURE 2. - Absorbance spectrum of Petrostep B-100 anionic surfactant.

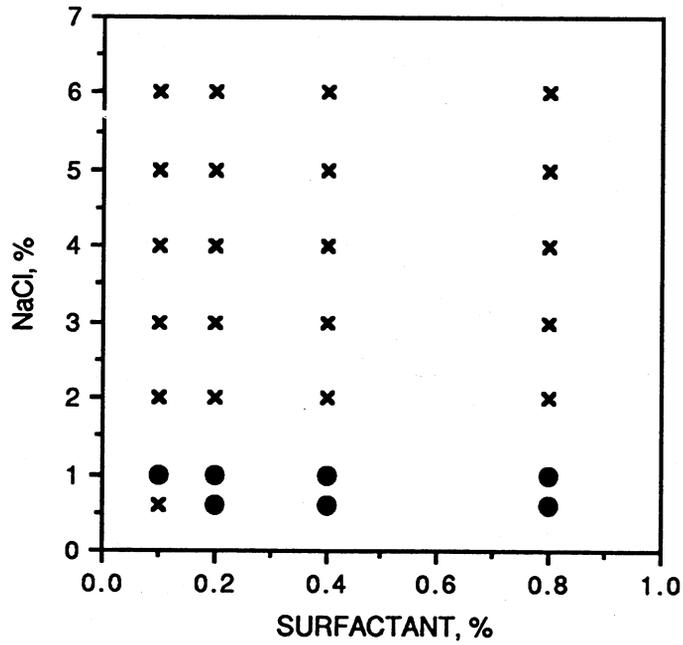


FIGURE 3. - Kern River crude oil phase behavior, pH 10.0, B-100 surfactant.

X = little or no interfacial activity, • = quality 3 or quality 4 emulsion.

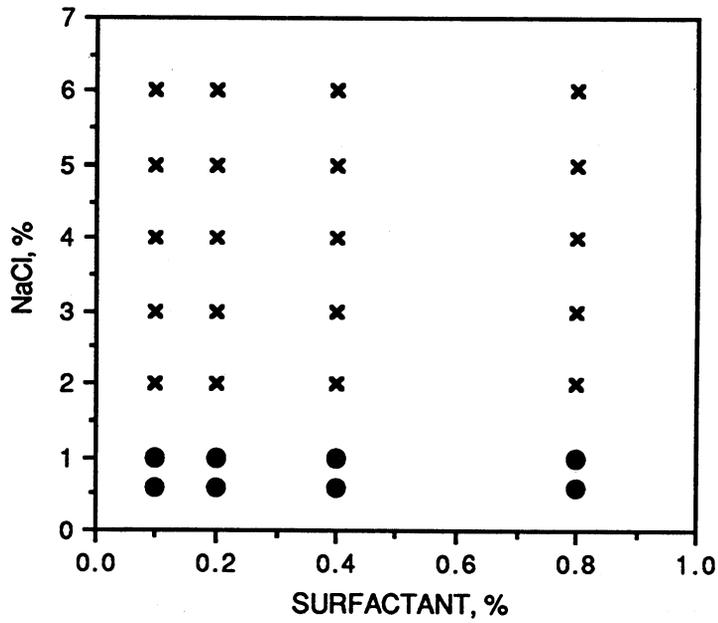


FIGURE 4. - Kern River crude oil phase behavior, pH 10.5, B-100 surfactant.  
 X = little or no interfacial activity, • = quality 3 or quality 4 emulsion.

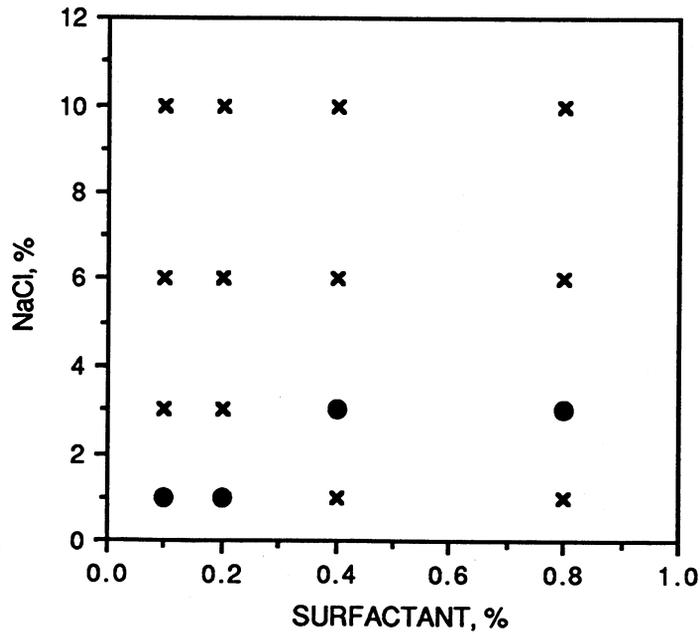


FIGURE 5. - Kern River crude oil phase behavior, pH 10.5, Neodol 25-9 surfactant.  
 X = little or no interfacial activity, • = quality 3 or quality 4 emulsion.

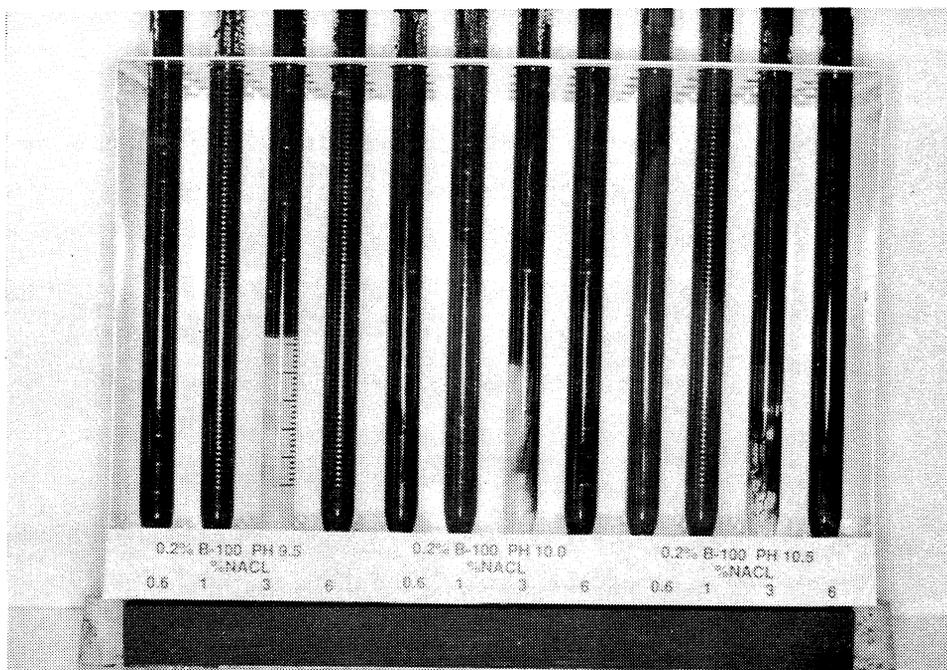


FIGURE 6. - Kern River phase behavior samples immediately after agitation, 0.2% B-100 surfactant.

correspond to high interfacial activity. The synergistic roles of surfactant and alkali in systems of this type was also reported previously.<sup>14</sup>

Similar activity (figure 5) was observed with Kern River oil and the Neodol 25-9 surfactant, except that the optimal salinity range was greater (up to 3% sodium chloride) and emulsions were produced only at pH 10.5.

The results of phase behavior tests with crude oil from the Ranger Zone of Wilmington (CA) oil field are shown in figures 7 through 10. The phosphate-containing B-100 formulation was interfacially active with the Wilmington oil only at pH 10.5 and from 0.6 to 1.0% sodium chloride concentration. Phase behavior was largely independent of surfactant concentration.

The phosphate-containing Neodol 25-9 surfactant formulation was interfacially active with the Wilmington oil at pH 9.5, 10.0, and 10.5. The maximum optimal sodium chloride concentration decreased from 10.0 to 6.0% as pH increased. This could be an effect of increasing carbonate concentration which results in increasing ionic strength in the alkaline solutions. At pH 10.0 and 10.5, the optimal salinity increased as surfactant concentration increased.

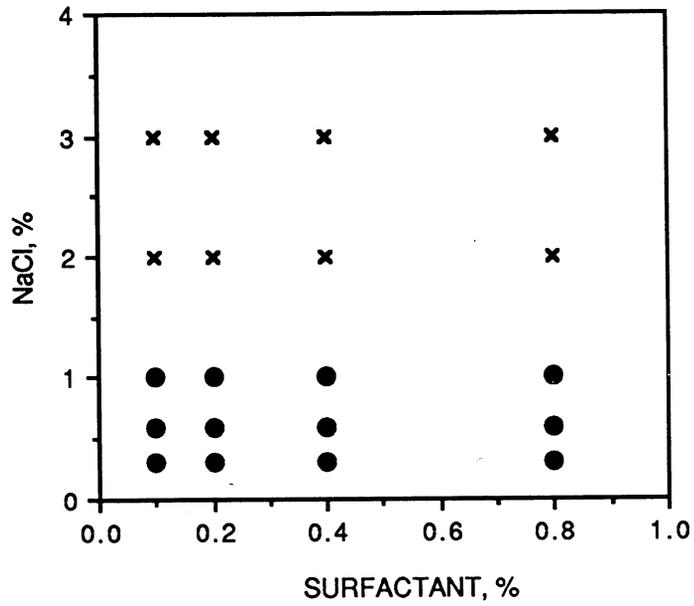


FIGURE 7. - Wilmington crude oil phase behavior, pH 10.5, B-100 surfactant.  
 X = little or no interfacial activity, • = quality 3 or quality 4 emulsion.

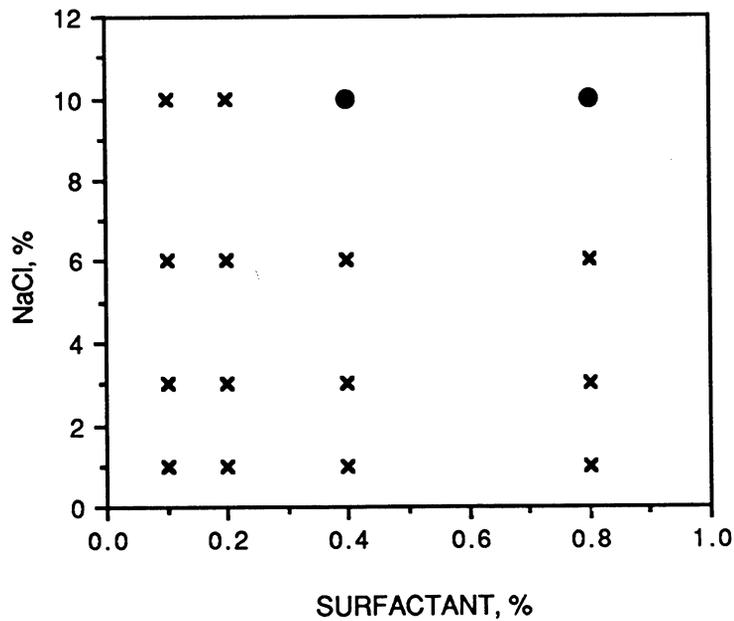


FIGURE 8. - Wilmington crude oil phase behavior, pH 9.5, Neodol 25-9 surfactant.  
 X = little or no interfacial activity, • = quality 3 or quality 4 emulsion.

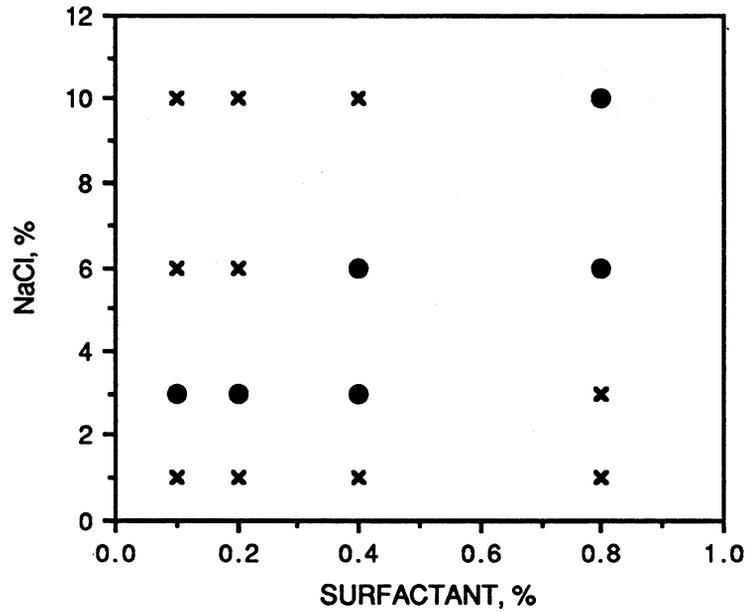


FIGURE 9. - Wilmington crude oil phase behavior, pH 10.0, Neodol 25-9 surfactant.  
 X = little or no interfacial activity, • = quality 3 or quality 4 emulsion.

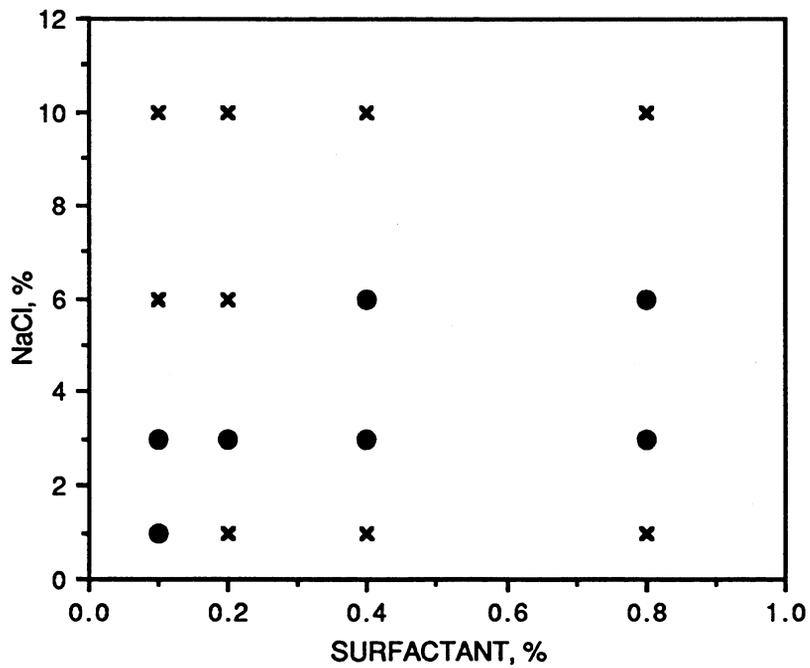


FIGURE 10. - Wilmington crude oil phase behavior, pH 10.5, Neodol 25-9 surfactant.  
 X = little or no interfacial activity, • = quality 3 or quality 4 emulsion.

In summary, the optimal salinities for producing interfacial activity with the Wilmington oil and the anionic surfactant were similar to those with the Kern River oil; however, the Kern River oil (highest acid number) was interfacially active at lower pH values than was the Wilmington oil. When the nonionic alcohol ethoxylate was tested, the optimal salinities were higher with the Wilmington oil than with the Kern River oil; however, the Wilmington oil, which had the lower acid number, was interfacially active at lower pH values than was the Kern River oil. It was concluded that a nonionic alcohol ethoxylate is more salt tolerant than an anionic surfactant, and that there is no direct correlation between TAN and conditions for producing interfacial activity with a phosphate-containing, surfactant-enhanced, low-pH alkaline system.

The experiments with the two heavier crude oils produced results that were in overall agreement with prior work performed with other heavy crude oils and alkali/surfactant systems.<sup>14</sup> It was discovered that a phosphate-containing, surfactant-enhanced, low-pH alkaline system produced interfacial activity with both heavy crude oils when optimal combinations of surfactant, salinity, and pH were used.

#### **Low TAN Oil**

The emulsions produced during the phase behavior tests with the low TAN crude oil were evaluated with different criteria than the emulsions produced with the moderate TAN oils. Emulsification of a low TAN crude oil caused emulsification behavior somewhat different from that observed with the other crudes. In general, the oil with a low TAN emulsified less easily and required more shaking to produce brown colored oil-in-water emulsions. Once a sample turned brown in color, further shaking never resulted in a change to a black color, as is often the case with unstable emulsions of other crude oils (demulsification). Therefore, primary evaluation of the emulsions was based on the stability of the emulsions after shaking.

The photograph shown in figure 11 is an example of the phase behavior observed with oil from Delaware-Childers (OK) oil field. The photograph is easily interpreted. For example, it can be seen that large quantities of a middle phase containing an oil-in-water emulsion were present at 0.1 and 0.2% surfactant concentration in the pH 9.5 sample tubes.

The Delaware-Childers oil was interfacially active with both surfactants at pH 9.5, 10.0, and 10.5 (see figures 12 through 17). Interfacial activity was independent of pH level and was dependent on surfactant concentration. The B-100 surfactant system was optimal between 0.3 to 1.0% sodium chloride concentration and 0.1 to 0.4% surfactant concentration. The N 25-9 surfactant system was optimal from 1.0 to 10.0% sodium chloride concentration and only at 0.8% surfactant concentration.

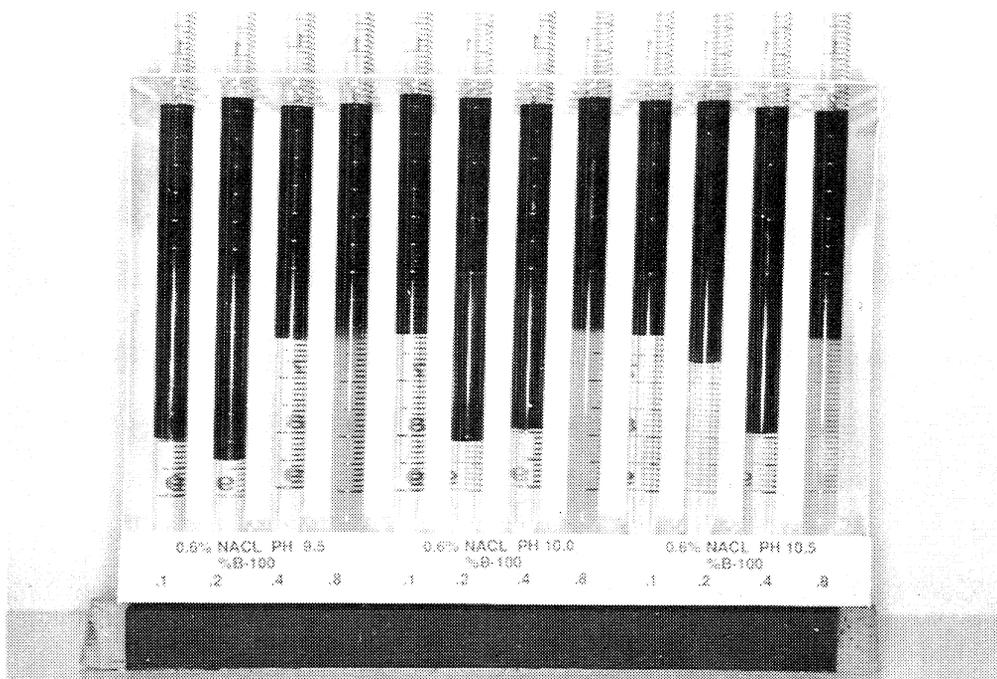


FIGURE 11. - Delaware-Childers phase behavior samples 1 day after agitation, 0.6% NaCl.

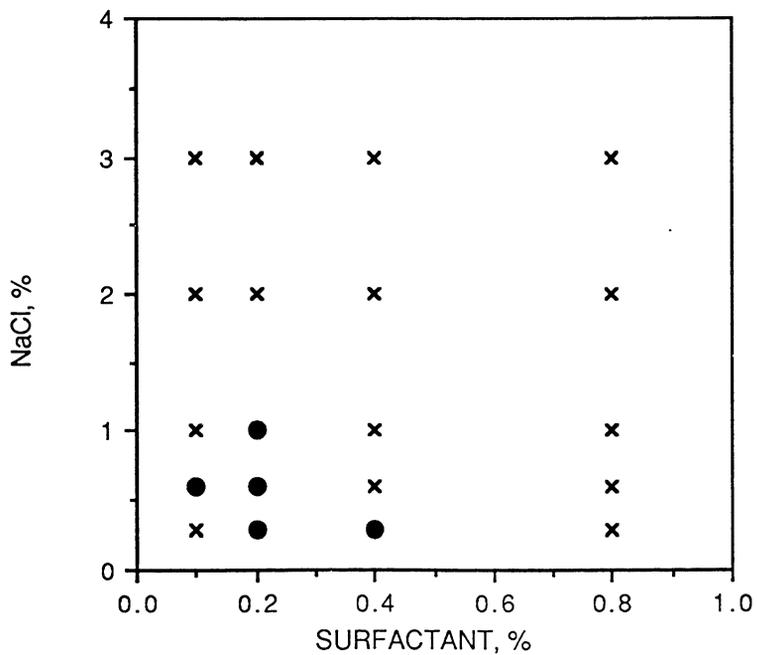


FIGURE 12. - Delaware-Childers crude oil phase behavior, pH 9.5, B-100 surfactant.  
 X = little or no interfacial activity, • = quality 3 or quality 4 emulsion.

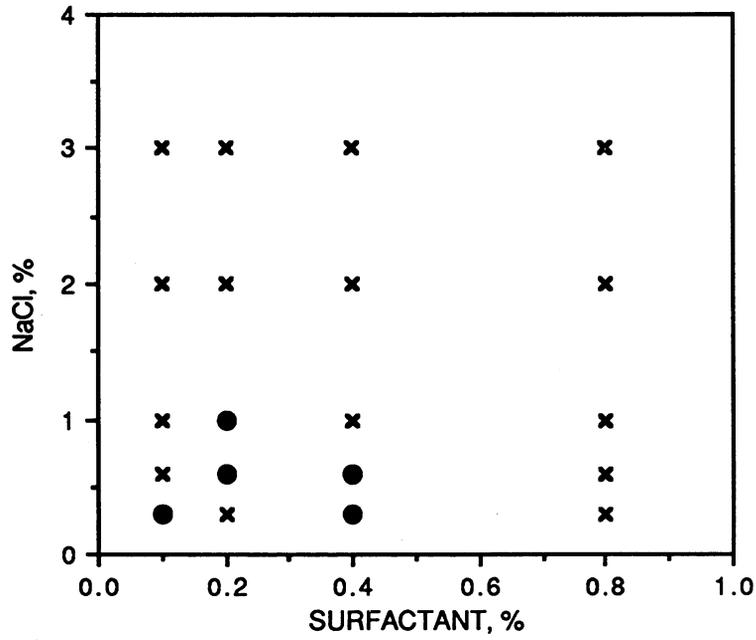


FIGURE 13. - Delaware-Childers crude oil phase behavior, pH 10.0, B-100 surfactant.  
 X = little or no interfacial activity, • = quality 3 or quality 4 emulsion.

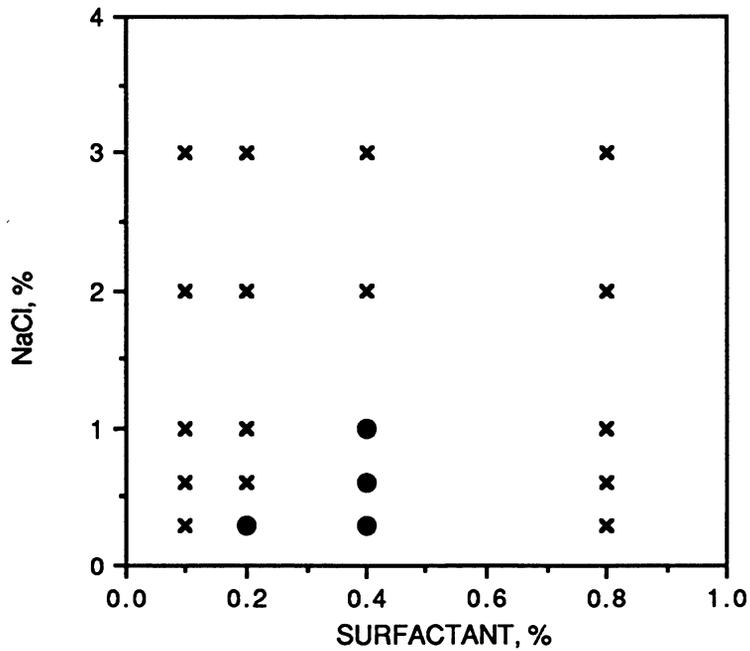


FIGURE 14. - Delaware-Childers crude oil phase behavior, pH 10.5, B-100 surfactant.  
 X = little or no interfacial activity, • = quality 3 or quality 4 emulsion.

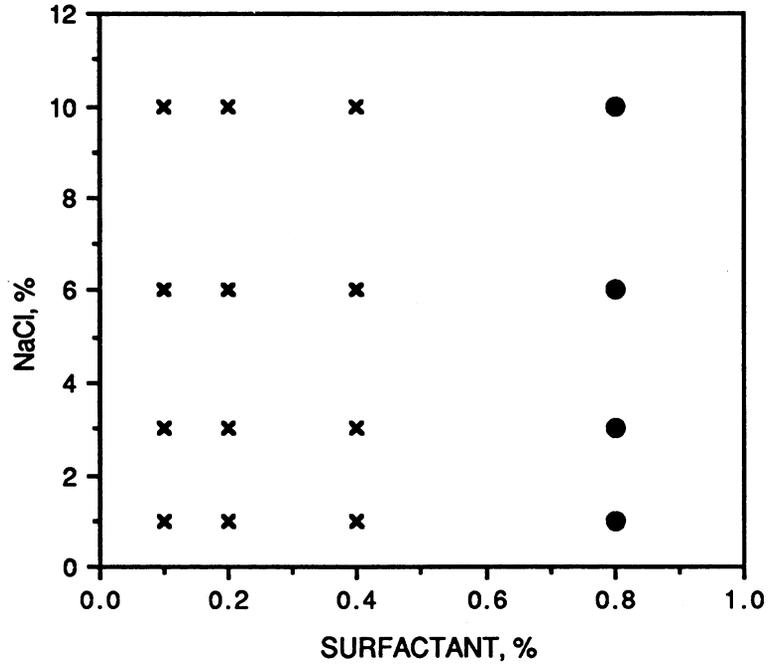


FIGURE 15. - Delaware-Childers crude oil phase behavior, pH 9.5, Neodol 25-9 surfactant.  
 X = little or no interfacial activity, ● = quality 3 or quality 4 emulsion.

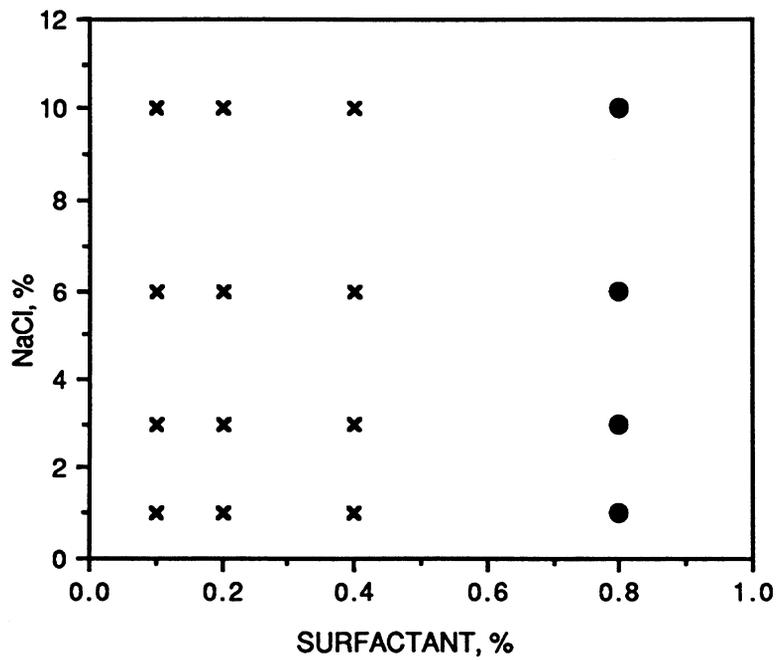


FIGURE 16. - Delaware-Childers crude oil phase behavior, pH 10.0, Neodol 25-9 surfactant.  
 X = little or no interfacial activity, ● = quality 3 or quality 4 emulsion.

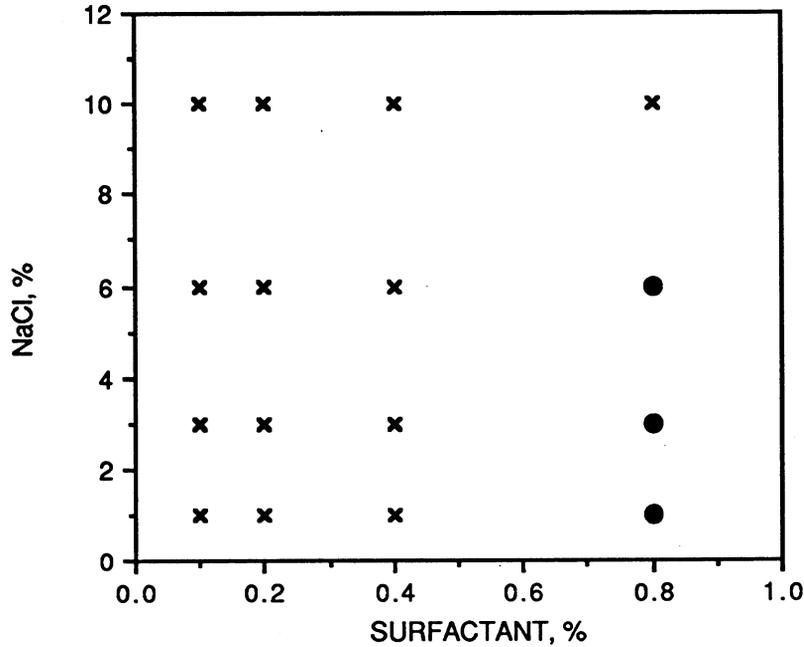


FIGURE 17. - Delaware-Childers crude oil phase behavior, pH 10.5, Neodol 25-9 surfactant.  
 X = little or no interfacial activity, • = quality 3 or quality 4 emulsion.

The oil with low TAN, Delaware-Childers, displayed interfacial activity at lower pH values than either of the other crude oils. It is not known if this was because this oil is naturally more reactive to synthetic surfactants, or if this result indicates that this lower acid oil contains some acidic components that are activated at low alkaline pH values. In either case, this demonstrates that surfactant-enhanced, low-pH alkaline systems do produce interfacial activity with a low TAN crude oil. This observation, which was initially based on visual observations of the emulsification tests, was confirmed by IFT measurements.

### Interfacial Tension

#### **Low TAN Oil**

The IFT experiments were conducted with a spinning-drop interfacial tensiometer, and the transient IFT behavior was monitored for several hours. The reactivity of the Delaware-Childers crude to alkaline conditions is shown in figure 18. This transient IFT experiment was conducted at pH 9.5 in 0.3% NaCl. Figure 18 shows that at pH 9.5, the oil is interfacially reactive to alkali; however, the reduction in IFT occurs at a very slow rate. After 16 hours of observation, the IFT between the alkaline aqueous solution and the oil was still greater than 2 mN / m, which is much too high to be expected to cause mobilization of residual oil. It was, therefore, concluded that alkali alone is not an effective chemical for enhanced recovery of this oil.

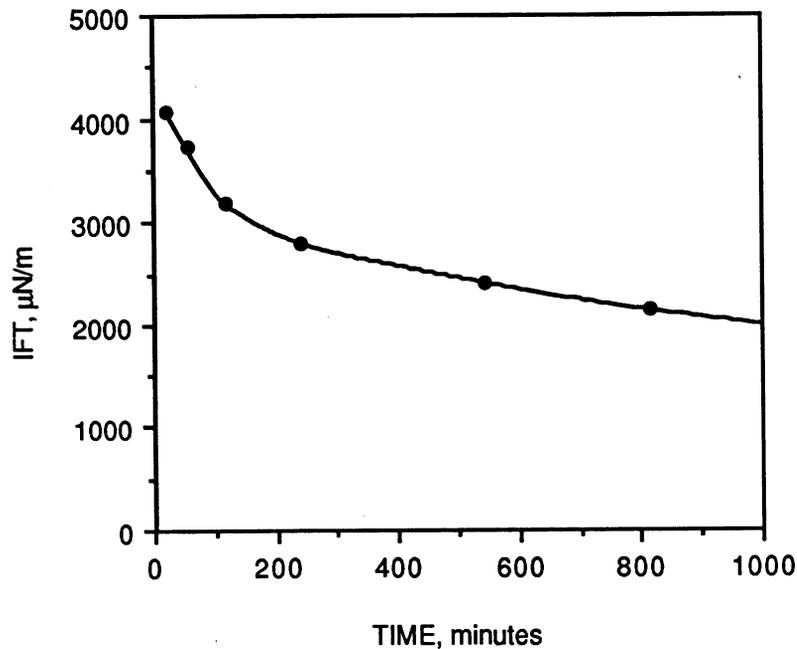


FIGURE 18. - Transient IFT behavior of Delaware-Childers crude oil, pH 9.5.

Figure 19 shows the transient IFT behavior of the Delaware-Childers oil with a solution of 0.4% Petrostep B-100, an anionic surfactant, in 0.3% NaCl. At this concentration of NaCl, high interfacial activity was observed at all three pH levels. The transient IFT behavior shown in figure 19 shows that the crude oil was interfacially reactive to the surfactant, but that the reduction in IFT occurred over a very long time. After 6 hours of measurement, the IFT with the anionic surfactant alone (unadjusted) was still above 1 mN/m.

Figure 19 also shows that increasing the pH of the system to 9.5 dramatically improved the IFT behavior. At pH 9.5, the IFT instantaneously decreased to below 10  $\mu\text{N/m}$  and remained below 10  $\mu\text{N/m}$  for 7 hours.

Similar results were obtained when using a nonionic surfactant, Neodol 25-9. The transient IFT data of an optimal system (0.8% surfactant in 3.0% NaCl) are shown in figure 20. When the pH of the system was increased to 9.5 or above, an immediate IFT reduction occurred; however, the minimum IFT did not reach the very low IFT value achieved with the other surfactant system.

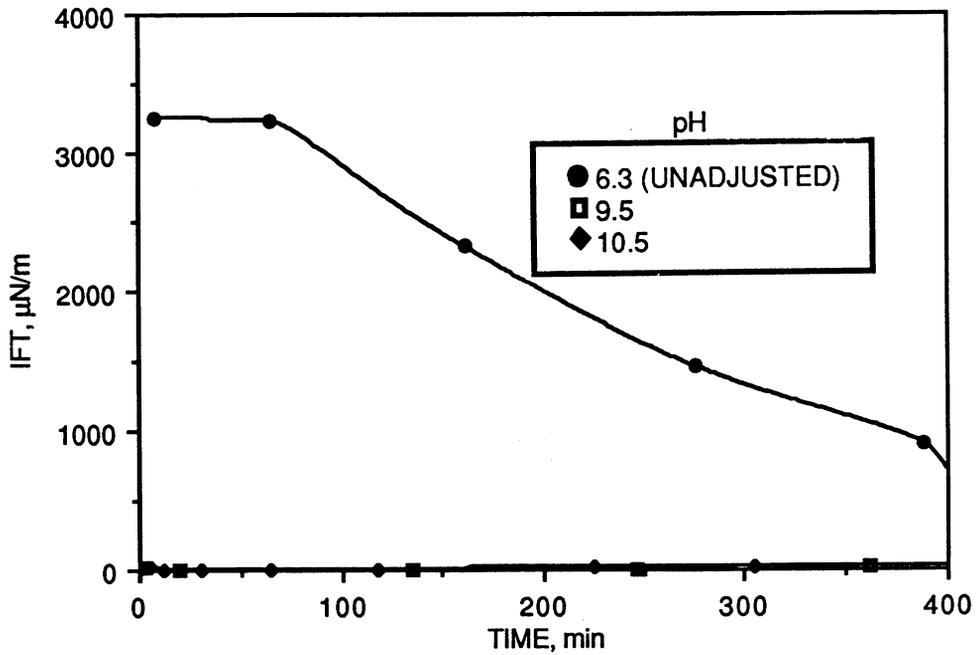


FIGURE 19. - Transient IFT behavior of Delaware-Childers crude oil and Petrostep B-100 surfactant.

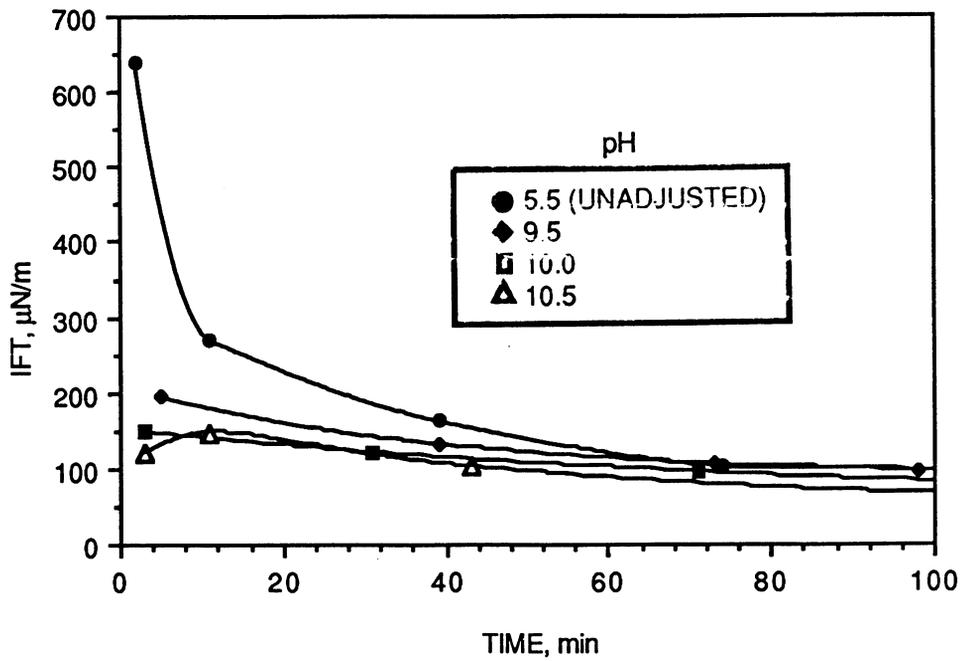


FIGURE 20. - Transient IFT behavior of Delaware-Childers crude oil and a nonionic surfactant.

The observations from transient IFT measurements with a low acid number crude oil are:

1. Alkali alone and surfactant alone reduced the IFT slowly.
2. Neither surfactant nor alkali alone were effective for achieving very low IFT.
3. Surfactant and alkali together reduced the IFT instantaneously.
4. Surfactant and alkali together produced low IFT that persisted over relatively long times.

### **Moderate TAN Oil**

#### **Comparison of Two Oil Samples**

Some experiments were performed this year using a sample of crude oil obtained from the Ranger Zone of Wilmington (CA) field. The current sample has a TAN of 1.6 mg/gm KOH and an API gravity of 18.0°. These oil properties are considerably different from the sample of Ranger Zone crude oil tested last year which has a TAN of 3.4 mg/gm KOH and an API gravity of 12.9°.

The transient IFT of the two oils are compared in figure 21. The IFT data for the FY88 oil sample was published previously.<sup>14</sup> The transient IFT behavior of the FY88 oil in a carbonate/surfactant system is nearly identical to the IFT behavior of the FY89 oil sample with the phosphate-containing surfactant system. This indicates that both oils react similarly despite the variation in the oil properties, and that addition of phosphate to the carbonate system has no deleterious effect on the transient IFT behavior of the alkaline/surfactant formulation.

#### **Effect of Divalent Ions**

One purpose of an alkaline preflush is to remove divalent cations from reservoir brine. Several preflush strategies have been previously tested and shown to be effective for reducing the divalent ion concentration in reservoir brines.<sup>14</sup> However, not all of the divalent ions are removed from the brine. The effect of the low concentrations of calcium ions on the transient IFT behavior of carbonate-phosphate-surfactant/Wilmington Ranger Zone crude oil was investigated at optimal conditions.

The experiments with carbonate-phosphate blends were conducted with two surfactants at pH 10 and pH 10.5. The surfactants were Neodol 25-9, a nonionic alcohol ethoxylate and Petrostep B-100, an anionic surfactant. The concentration in each case was 0.1% surfactant. The Neodol system was tested at 3.0% NaCl concentration, and the Petrostep system was tested at 0.3% NaCl concentration. The concentrations of calcium ions in the brines were 0, 10, and 100 ppm. At 100 ppm, the solution contained

precipitate which indicates that, at that concentration, the system is in an equilibrium state similar to a reservoir that has been preflushed with alkali to precipitate divalent ions to the extent possible.

The transient IFT behavior of the nonionic surfactant with Wilmington Ranger Zone crude oil is shown in figure 22. The initial IFT and the rate of IFT increase is very nearly equal with and without low levels of calcium ions present. (Note that the 100 ppm calcium ion level is, as stated above, actually a much lower calcium concentration than 100 ppm due to precipitation that occurred as a result of reaction with carbonate ions.) There is a clear correlation for somewhat higher final IFT values when calcium ions are present in the system.

The transient IFT behavior of the anionic surfactant is shown in figure 23. In this figure, there is not a clear correlation between initial or final IFT values and calcium ion concentrations.

The results from both IFT experiments showed that the transient IFT behavior was little affected by the presence of calcium ions. Since the calcium had little effect, even when the concentration was high enough to cause precipitation, it appears that the low levels of divalent ions that remain after a reservoir preflush are not detrimental to the IFT behavior of surfactant-enhanced alkaline systems and crude oil.

### **Surfactant Loss**

#### **Bottle Adsorption Tests**

Bottle adsorption tests (table 4) confirmed that a pH 10.0 alkaline solution, containing carbonate and phosphate, was effective for reducing Petrostep B-100 surfactant losses on crushed (particle diameters from 250 to 425  $\mu\text{m}$ ), unfired, Berea sandstone. The effect of the alkaline chemicals was to reduce surfactant loss in the crushed Berea by 22%. These results are in agreement with previous results obtained with carbonate at similar pH levels.<sup>15</sup>

#### **Filtration Tests**

Filtration experiments were performed to obtain a better understanding of the effects of NaCl and pH adjustment on the behavior of the surfactant. Some cloudiness was observed in all the surfactant solutions. The test results, (table 5), showed that the presence of both NaCl and alkali significantly reduced the filterability of the surfactant solution. In distilled water, 94.1% of the surfactant passed through a 0.45- $\mu\text{m}$  filter. After addition of 0.3% NaCl, 68.2% of the surfactant passed through the filter. Adjustment of the pH to 10.0 reduced the amount of surfactant that passed through the filter to 7.7%. When the pH 10.0 surfactant solution was heated above 45° C, the solution became less cloudy, and the filterability of the solution was improved.

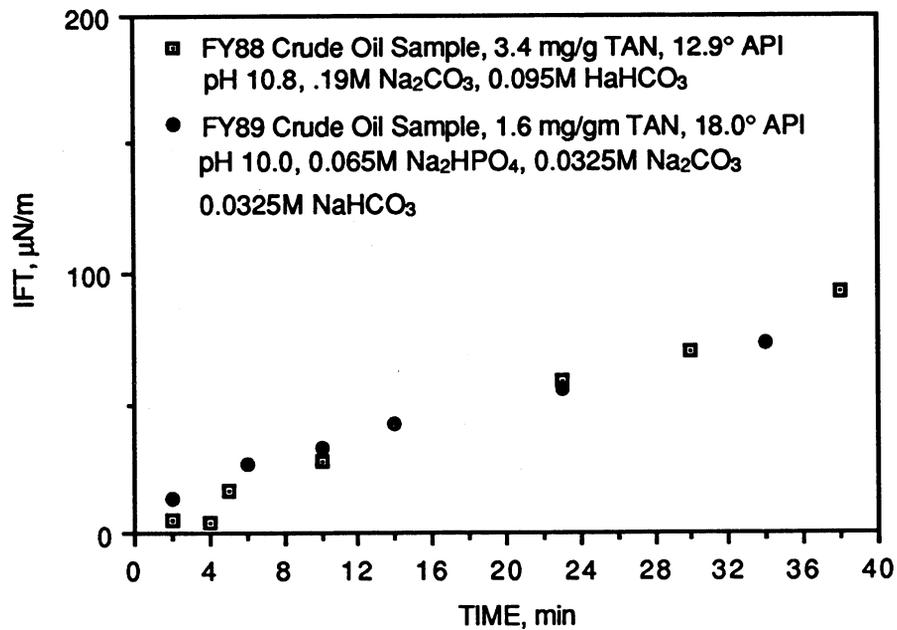


FIGURE 21.-Transient IFT behavior of FY88 and FY89 Wilmington Ranger Zone oil samples, Neodol 25-9 surfactant, 52° C.

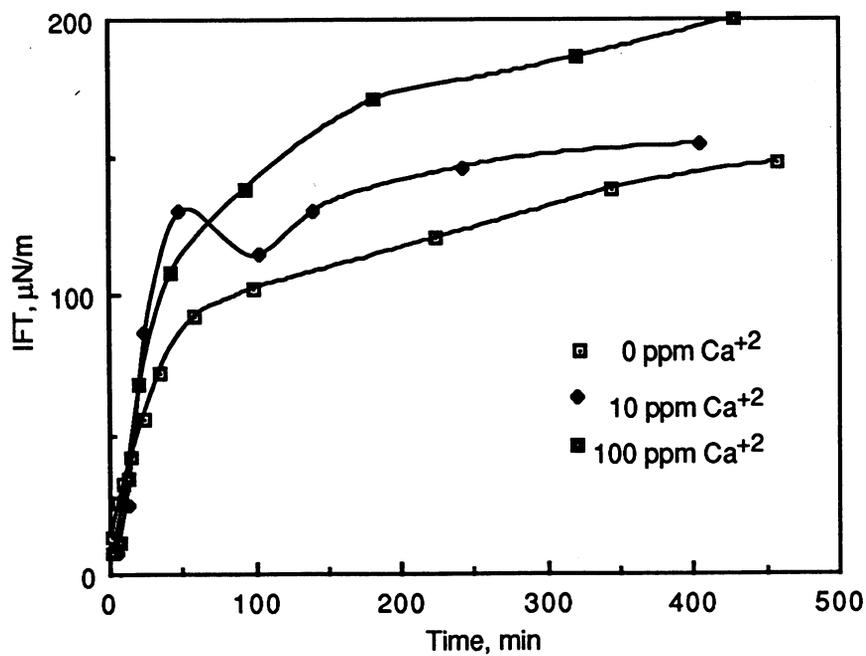


FIGURE 22. - Transient IFT of Wilmington crude oil, 0.1% Neodol 25-9, 3.0% NaCl, and Ca<sup>+2</sup>, pH 10.0, 52° C.

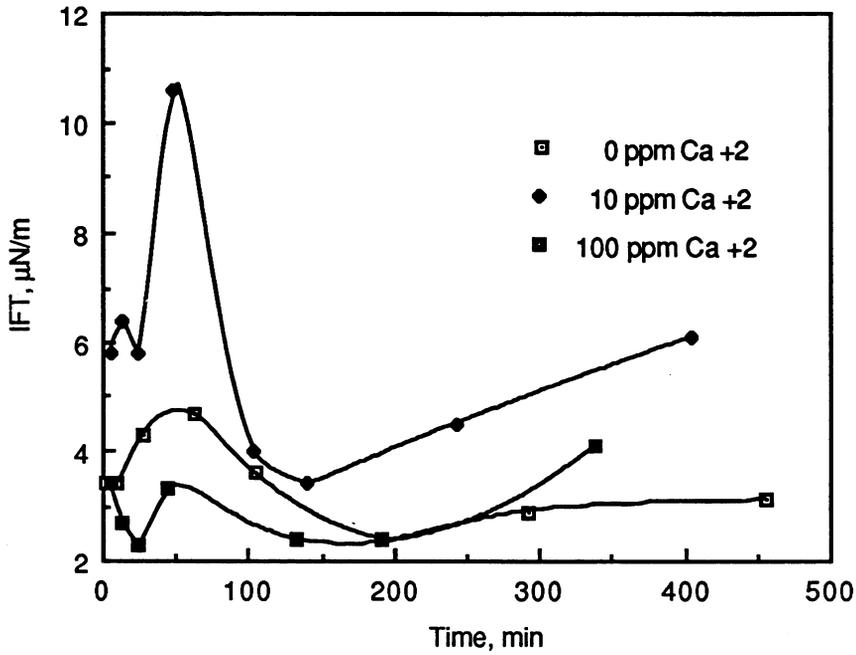


FIGURE 23. - Transient IFT of Wilmington crude oil, 0.1% Petrostep B-100, 0.3% NaCl, and Ca<sup>+2</sup>, pH 10.5, 52° C.

TABLE 4. - Surfactant loss in crushed Berea sandstone, 0.1% Petrostep B-100, anionic surfactant, 25° C

pH	NaCl, %	Adsorption, meq/kg
6.3	0.3	1.074
6.3	0.3	1.050
10.0	0.3	0.844
10.0	0.3	0.823
6.3	0.0	0.649
6.3	0.0	0.675
10	0.0	0.589
10	0.0	0.576

TABLE 5. - Filtration of 0.1% Petrostep B-100 anionic surfactant

Temp, °C	pH	NaCl, %	Filter size, μm	Passed through filter, %
25	6.3	0	0.1	68.8
25	6.3	0	0.45	94.1
25	10.0	0	0.1	2.0
25	10.0	0	0.45	40.3
25	6.3	0.3	0.1	39.5
25	6.3	0.3	0.45	68.2
25	10.0	0.3	0.1	3.5
25	10.0	0.3	0.45	7.7
50	6.3	0.3	0.45	98.1
50	10.0	0.3	0.45	22.1

The 0.45-μm filter has much smaller pores than the mean pore throat radius of 2.6 μm calculated for a 36-md Berea core. However, these data do indicate that surfactant particles can change size, depending on pH and salinity. This factor could be important in some flooding situations and may play a role in high surfactant loss in corefloods when high adsorption is not expected.

#### Surfactant Transport in Porous Media

The transport of Petrostep B-100 surfactant in oil-free Berea cores was studied at 23° and 52° C. The results of the corefloods are summarized in table 6. The results are useful for correlating surfactant transport with temperature, pH, permeability, and ionic strength.

It was discovered that it was not possible to propagate the surfactant at 0.1% concentration through the low-permeability cores. These experiments were performed at pH 6.3 (natural pH) and pH 10.2 at ambient (23° C) temperature. The pH 10.2 solution had a measured alkalinity of 0.1866 meq/mL and a surfactant concentration of 0.00256 meq/mL. The results of the effluent analyses are shown in figures 24 and 25. In neither case was any significant concentration of surfactant found in the effluent fractions. Both cores had initial permeabilities below 40 md. The final permeability of each core was 63% lower than the initial permeability. The loss of surfactant in low permeability cores was much greater than expected. The loss of surfactant in these low-permeability cores is believed to be a filtration effect.

When high-permeability (500 md) cores were used, surfactant was transported through the cores. These experiments were performed at 23° with a chemical slug that contained 0.00256 meq/mL of surfactant and 0.1866 meq/mL of alkalinity, and at 52° C with a chemical slug that contained 0.00293

meq/mL of surfactant and 0.1756 meq/mL of alkalinity. At pH 10.2, increasing the core temperature from 23° to 52° C caused very little change in the amount of surfactant permanently retained in the cores. At 23° C, 0.198 meq/kg of surfactant was retained; at 50° C, 0.186 meq/kg was retained. It is not surprising

TABLE 6. - Injection of 0.1% Petrostep B-100 surfactant into unfired Berea cores

Coreflood	Temp., °C	Frontal advance ft/d	Chemical Slug		Permeability, md		Chemical injected <sup>2</sup> , meq/kg		Chemical loss <sup>2</sup> , meq/kg	
			volume, PV	pH	Initial	Final	Alkali	Surfactant	Alkali	Surfactant
1	23	0.40	1.40	10.17	19.6	7.2	20.61	.286	1.51	All <sup>1</sup>
2	23	0.40	0.97	6.3	36.3	13.5	0	.197	-	All <sup>1</sup>
3	23	0.47	1.05	10.17	508	331	21.89	.301	1.91	0.198
4	52	0.59	1.40	10.17	502	400	28.57	.477	1.31	0.186
5	52	0.55	1.31	6.3	554	435	0	.408	-	0.375

<sup>1</sup>All the injected surfactant was retained in the core.

<sup>2</sup>Per kg of rock.

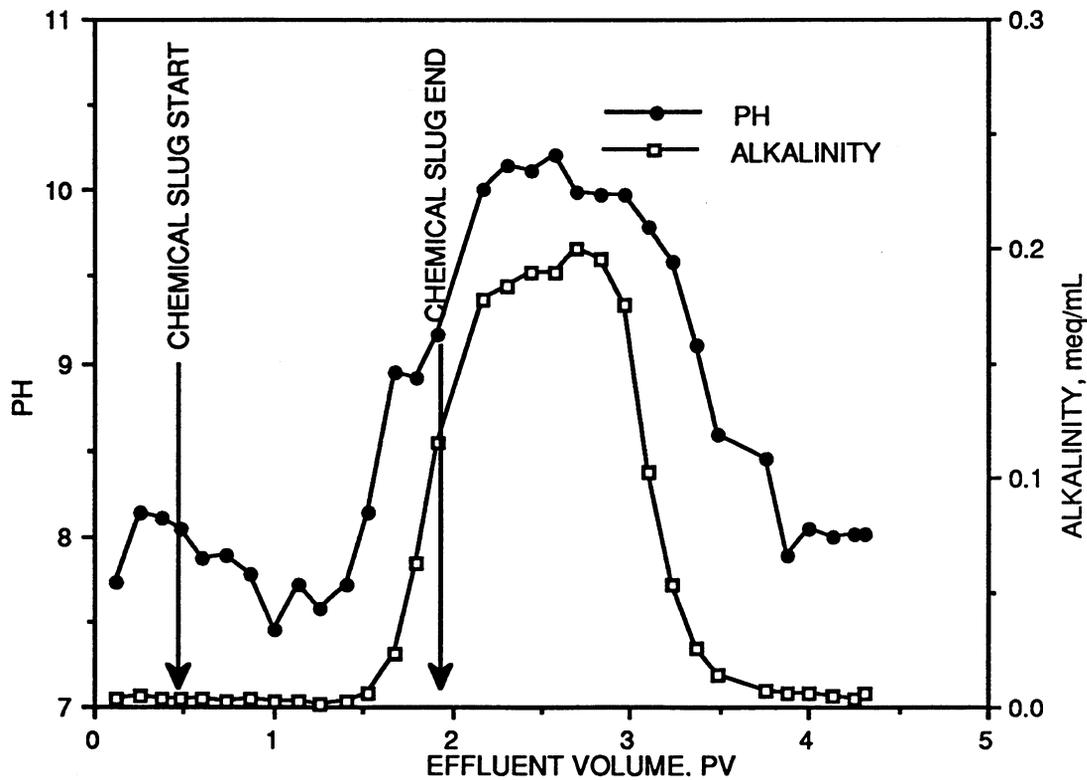


FIGURE 24. - Coreflood 1 (23° C) effluent analyses - pH and alkalinity.

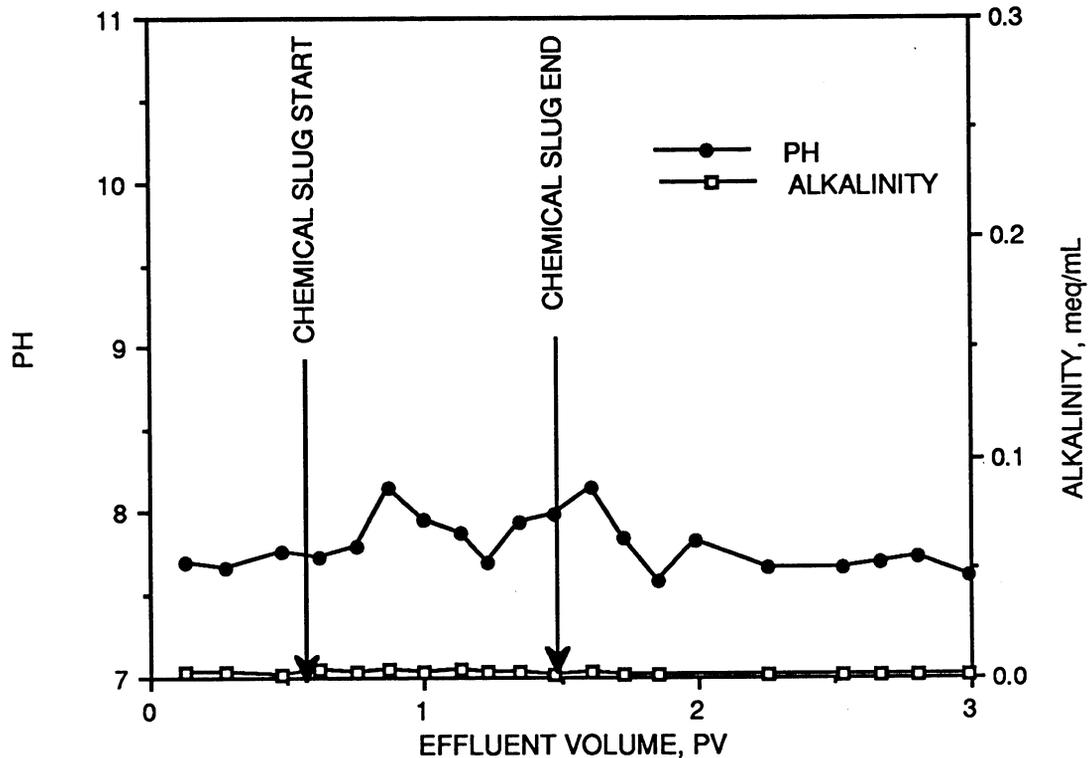


FIGURE 25. - Coreflood 2 (23° C) effluent analyses - pH and alkalinity.

that surfactant retention was not a lot less at 52° C than at 23° C because prior results have shown only moderate reductions in surfactant adsorption over the 23° C to 70° C temperature range.<sup>15</sup> There was, however, a marked difference in the rate at which the surfactant was transported through the cores.

At the lower temperature (23° C), there was a lag of 0.89 PV beyond the point at which the surfactant should have shown up in the effluent (fig. 26). Surfactant should have emerged from the core about 1 PV after chemical slug injection began; but instead, showed up 1.93 PV after starting surfactant injection.

At the higher temperature (52° C), surfactant showed up in the effluent 0.99 PV after chemical slug injection began (fig. 27). However, there was a large increase in surfactant concentration 0.78 PV after chemical slug injection was completed. This shows that, even at the higher temperature, propagation of surfactant through the core was partially delayed, presumably by the adsorption.

Further examination of figures 26 and 27 reveals that in addition to permeability and temperature, changing ionic strength probably also plays a role in the rate at which the surfactant is transported through the cores. At 23° C, surfactant showed up in the effluent 0.89 PV after injection of surfactant solution was

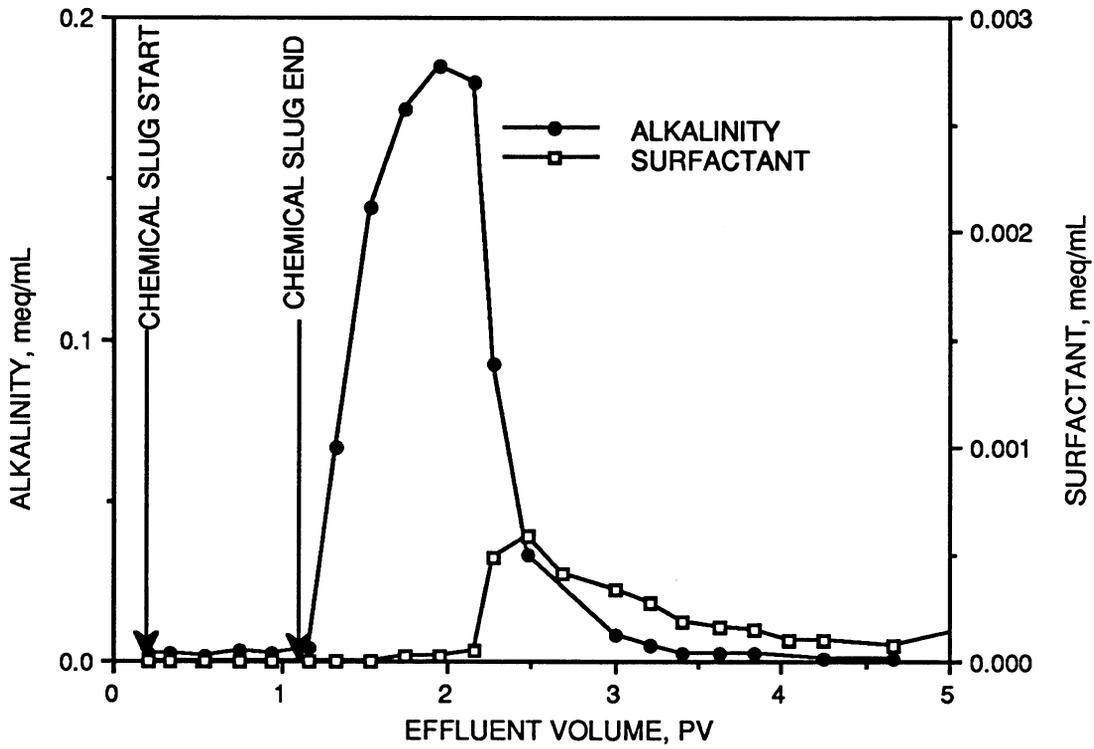


FIGURE 26. - Coreflood 3 (23° C) effluent analyses - alkalinity and surfactant.

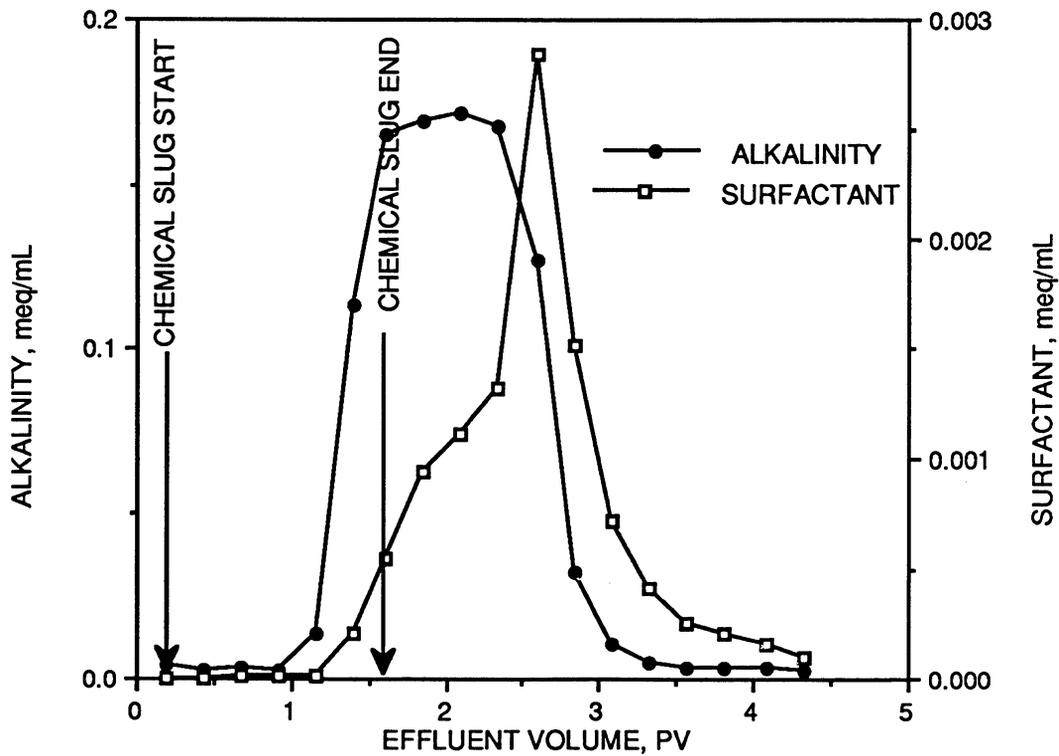


FIGURE 27. - Coreflood 4 (52° C) effluent analyses - alkalinity and surfactant.

terminated. At 52° C, surfactant showed up in the effluent 0.99 PV after chemical slug injection was begun; however, there was another peak of high surfactant concentration at 0.78 PV after chemical injection was terminated. These observations indicate that surfactant transport is also affected by ionic strength, since the surfactant formulation contains alkaline agents in addition to NaCl and is, therefore, of higher ionic strength than the 0.3% NaCl that was used as a drive fluid.

Even though the shape and timing of the surfactant effluent analysis graphs (figs. 26 and 27) indicate that surfactant transport is partly determined by filtration effects occurring in the core, the total amount of surfactant retained in the cores at pH 10.2 is low. The average retention of  $0.192 \pm 0.06$  meq/kg sandstone is 40 to 70% less than abstraction values previously reported in reservoir sandstones.<sup>3, 14</sup>

For comparison, a similar coreflood was performed at pH 6.3 in a high-permeability (554 md) core. The results are given in figure 28. Surfactant showed up in the effluent about 1.05 PV after slug injection was begun, however 95% of the injected surfactant was permanently retained in the core, presumably by adsorption at the lower pH level. Comparison of the surfactant adsorption in cores 4 and 5 reveals that surfactant loss in the core was reduced by 50.4% when the pH was increased from pH 6.3 to pH 10.2 (see table 1).

The five corefloods reveal that surfactant transport through porous media is improved by increasing permeability, temperature, and pH and by decreasing total ionic strength.

### **Alkali Consumption**

Alkali consumption in the 23° and 52° C corefloods averaged  $1.6 \pm 0.2$  meq/kg sandstone. In the low-permeability (20 md) core (coreflood 1), alkali showed up in the effluent 0.99 PV after chemical slug injection was begun (fig. 29). In the high-permeability (500 md) cores, alkali was detected in the effluent  $0.91 \pm 0.01$  PV after chemical slug injection was begun (figs. 25 and 26). This indicates more dispersion in the high-permeability cores.

The effluent pH curves for corefloods 3 and 4 are shown in figure 29. At 52° C, the effluent pH did not reach the pH of the injected chemicals. The consumption of alkali in the Berea cores was low and scarcely affected by temperature or permeability. It is not surprising that increasing the temperature did not increase alkali consumption because it was previously shown that, in this pH range, alkali consumption reactions occur rapidly with little further reaction after the initial reactions.<sup>14</sup>

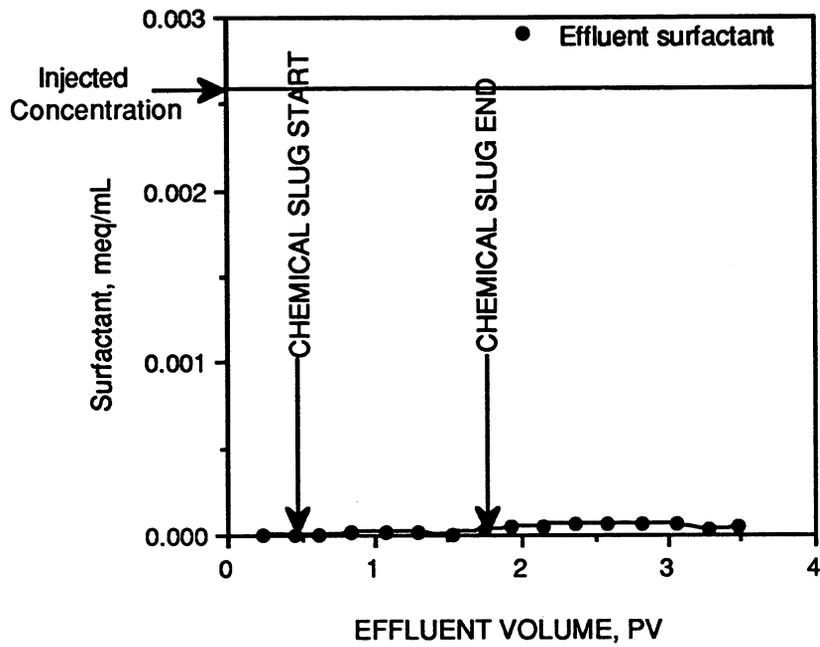


FIGURE 28. - Coreflood 5 (52° C) effluent analysis - surfactant.

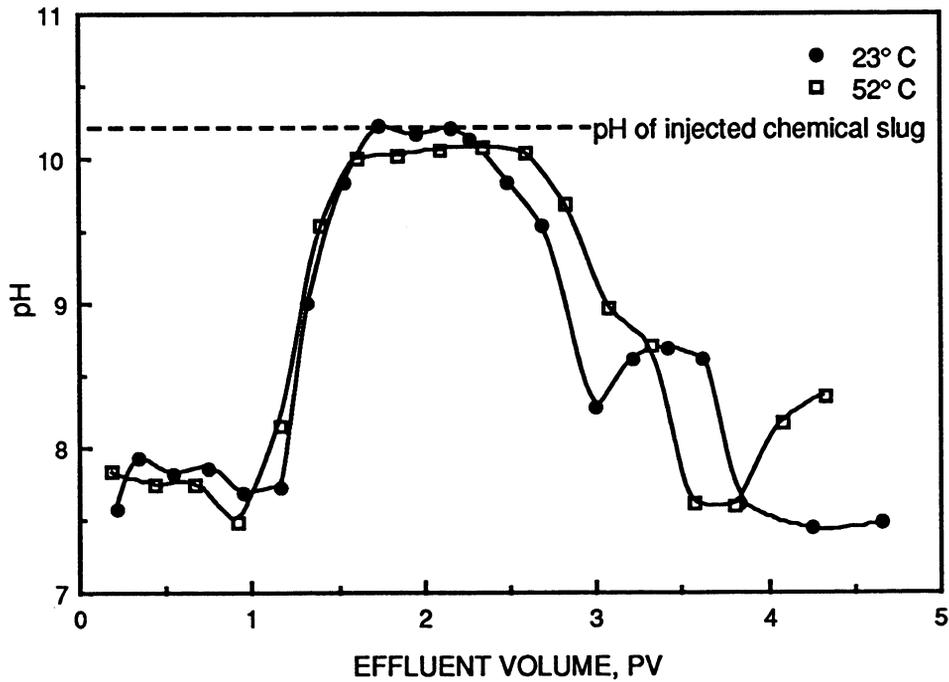


FIGURE 29. - Effluent pH - corefloods 3 and 4.

## **OBSERVATIONS, RECOMMENDATIONS AND CONCLUSIONS**

### **Observations**

1. A phosphate-containing surfactant-enhanced alkaline chemical system produced interfacial activity with crude oils having total acid numbers that vary from very low to moderate.
2. Low levels of calcium ions had no detrimental effect on the IFT behavior of surfactant-enhanced alkaline formulations that contain added monohydrogen phosphate ions.
3. The size of surfactant aggregates appeared to change size, depending on pH and total ionic strength, and this phenomena may be important in some flooding situations.
4. The transport of surfactant through porous media improved when pH, permeability, and temperature were increased.
5. High total ionic strength had an adverse effect on the transport of surfactant through porous media.
6. Alkali consumption at pH 10.2 in Berea cores was low.

### **Recommendations**

1. Perform one coreflood in an oil-free core with a pH 10 surfactant solution that is followed by a chase solution of equal ionic strength.
2. Monitor surfactant transport through cores that contain residual oil.

### **Conclusions**

1. The potential target resource for surfactant-enhanced alkaline flooding may extend to crude oils having very low total acid numbers.
2. The effects of permeability, ionic strength, and temperature on surfactant transport are believed to be related to the size of the surfactant particles.
3. The effect of pH on surfactant transport is believed to be due to changes in surfactant adsorption.
4. Surfactant transport in reservoirs that are heterogeneous in permeability and salinity may not correlate with fluid flow patterns unless the chemical system is carefully designed.

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