

Topical Report
BICARBONATE IN CHEMICAL FLOODING

Prepared by

Deborah A. Peru
Philip B. Lorenz

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NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH

A Division IITRI
P. O. BOX 2128
BARTLESVILLE, OKLAHOMA 74005
(918) 336-2400

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SUMMARY

The objective of the work that NIPER has performed under the cooperative research program OE3C, was to evaluate the effectiveness of sodium bicarbonate as a chemical for enhanced oil recovery.

The experimentation consisted of determining the stability of emulsions formed with sodium bicarbonate and oil. The stability was monitored as a function of pH and salinity and was compared to the stability of emulsions formed with sodium chloride and sodium carbonate. Wettability tests were done to determine the affect of sodium bicarbonate on the wetting of Berea sandstone. Finally, laboratory corefloods were run to determine the amount of tertiary recovery using sodium bicarbonate.

The conclusions drawn from this six-month research program are:

1. Sodium bicarbonate can recover tertiary oil. With optimization of the chemical slug a sufficient amount of oil should be recovered that might interest oil producers.
2. Sodium bicarbonate altered the wettability of Berea sandstone from water-wet to oil-wet (Cerro-Negro crude).
3. Sodium bicarbonate reduced the stability of emulsions that has been a deterrent to the success of surfactant flooding.

Key Words

Emulsification/Demulsification Tests: Formation of an emulsion which is monitored for stability by measuring the volume of brine which separates from the emulsion and settles to the bottom of the calibrated test tube. Stability is inversely proportional to the volume of brine. These tests come under Task 1 called "Screening Tests".

Layer Volume Fraction: The volume of brine, oil or emulsion divided by the total volume in the test tube.

Acid Number: mg KOH/g oil sample. Determined by a potentiometric titration of the oil with standardized KOH. The end point is at the inflection in the titration curve. Values reported are total acidic components of weak and strong acids.

Wettability: A preferential affinity of reservoir rock to either water or oil where both are present. A change in wettability comes about by a change in the affinity of the oil for the rock surfaces and a change in affinity of the rock surface for the oil. Wettability numbers reported are on a scale of -1 to +1. Zero (0) is neutral, -1 is very oil wet, and +1 is very H₂O wet.

Coalescence: The uniting of dispersed droplets into one body of oil or water. The coalescence of droplets breaks emulsions (demulsification).

Salinity: The total ionic strength of all electrolytes (NaCl, NaHCO₃, Na₂CO₃).

INTRODUCTION

Sodium bicarbonate, NaHCO_3 , is a weak alkaline chemical. Since the extent of dissociation is small (2.34×10^{-8}), bicarbonate is able to buffer a solution quite well over a hydrogen concentration range of 10^{-2}M . Therefore, it is not expected that sodium bicarbonate would react with oil and rock in all the same ways that conventional alkaline agents do.

In many cases, the primary mechanism of an alkaline flood process is for the alkaline solution to react with the acid components in the crude oil thereby producing surfactants in situ. These surfactants should lower interfacial tension and therefore improve mobilization of the oil. Another mechanism associated with alkaline flooding is an alteration in wettability of the reservoir rock. However, the commonly used alkaline solutions are strongly dissociated producing a local pH of 12-14. Therefore, several problems can arise, such as mineral dissolution and precipitates with divalent ions which can lead to plugging in the well bore.

The bicarbonate ion has a pH of 8.0-8.3, depending upon the salts dissolved in the solution. Although this is probably too low to produce surfactants in situ, bicarbonate has the potential of decreasing the formation of stable emulsions, altering the wettability of reservoir rock, and lowering interfacial viscosity by buffering the interface and bulk phase at the same pH (1).

In accordance with the contract, three tasks were performed. Task 1 was to perform screening tests on various crude oils to determine if sodium bicarbonate is effective in forming emulsions that demulsify rapidly enough to form an oil bank. Sodium bicarbonate was compared with sodium chloride and sodium carbonate. Task 2 was to determine if sodium bicarbonate creates the wettability reversal characteristic of conventional alkaline agents. Task 3 was to perform coreflooding experiments with sodium bicarbonate, to test its effectiveness in enhanced oil recovery. This report is divided chronologically into three sections. Section A gives results predominantly from Task 1, September through November. Section B gives the results on Tasks 1 and 2, November through January. Section C gives the results on Task 2 and 3, January through February. Each section will end with a conclusion on the work done during that time frame.

SECTION A

Tests were made of emulsification and coalescence with heavy crude oils in brines of plain sodium chloride, sodium carbonate plus sodium chloride, and sodium bicarbonate plus sodium chloride. Two of the oils, Midway-Sunset #76067 and Wilmington #77032, are from the Bureau of Mines analysis program. The results of the analysis are given in table 1a. The Wilmington oil #5-G was collected from a different well in a different year, and was allowed to sit for several years. The Noone oil #80002 was obtained from Logan, KS. Delaware-Childers oil obtained in Nowata, OK was used as a diluent in some of the studies.

Experimental

Chemicals and Equipment

Centrifuge tubes 13 and 15 ml graduated with screw caps
Nitrogen gas
Deionized water
Various heavy crude oils
Sodium chloride (Fischer certified)
Sodium bicarbonate (Fischer certified)
Sodium carbonate (Fischer certified)
10 ml serological pipettes sealed at both ends with an oxygen flame

Procedure

All experiments were conducted at an oil/brine volumetric ratio of 1. When the oil/brine mixtures were in the graduated centrifuge tubes, the air space was flushed with nitrogen gas for 30 seconds and the tubes were capped. Each tube was then shaken for three minutes. Three rounds of one minute/tube was found to be satisfactory for creating emulsions. The test tubes were set vertically and the volumes of oil, water, and emulsion layers observed as a function of time.

It should be noted that the Wilmington #5-G and Noone oil #80002 were diluted 1:2 with Delaware-Childers oil to produce an acid oil of moderate viscosity which permitted emulsification by hand at room temperature. The Wilmington #77032 was not diluted and was emulsified at room temperature (78° F) for one hour by a Burrell wrist action shaker. The Midway-Sunset #76067 was not diluted and was emulsified at 122° F by hand for a total of three minutes/tube.

TABLE 1a. - Properties of crude oils

Oil	Gravity, 60° F			S	N	C Res.	Acid Number mg of KOH/g oil	Residue* vol. %
	Spec. g/cm ³	API deg						
Wilmington B77032	0.967	14.8		2.18	0.672	17.6	2.31	49.0
Midway-Sunset B76067	0.970	14.4		1.05	0.732	14.7	4.15	51.1

*Temperature >572° F; Pressure = 40 mmHg

Experimental Results

The most favorable behavior with alkaline agents is the formation of an oil-in-water (o/w) emulsion ("emulsification and entrainment") that subsequently coalesces. Also, coalescence of water-in-oil (w/o) emulsions is desirable. It would be premature to draw definitive conclusions about the effect of bicarbonate, especially as emulsion characteristics depended on oil type and salinity.

The results presented in figures 1-7 are representative of the data acquired.

Effect of brine on emulsion stability

In figures 1a and 2a, the Wilmington #77032 and Midway-Sunset #76067 oils formed w/o emulsions with 1 percent NaCl that showed no sign of coalescing. Figure 3a, on the other hand, shows that the Noone oil #80002 emulsified the brine completely at first, but it was 80% coalesced after 240 hours.

The effect of bicarbonate was:

Wilmington #77032: No significant amount of emulsion after 20 hours.

Midway-Sunset #76067: An oil layer and two stable emulsion layers (w/o and o/w) after 70 hours.

Noone #80002: Faster coalescence than with plain brine, 100% complete at 260 hours.

In contrast, carbonate had an unfavorable effect on the above oils:

- Wilmington #77032: Two stable emulsion layers (w/o and o/w) after 40 hours.
- Midway-Sunset #76067: Two emulsion layers; w/o decreasing with time, o/w increasing but no coalescing.
- Noone #80002: 98% w/o emulsion, very stable.

Salinity Effect

Figure 4a gives a set of curves for the Wilmington oil #5-G. The water/oil emulsions were progressively more stable as salinity increased.

Figures 5a and 6a for Midway-Sunset and Noone oils show that the effect of salinity is not always straightforward; however, higher salinity usually increased w/o emulsification. The effect was counteracted by the presence of bicarbonate.

pH Effect

Figure 7a shows that mixing carbonate and bicarbonate resulted in a regular progression of layer volumes with Noone oil, such that w/o emulsification increased with decreasing proportions of bicarbonate.

Conclusions

In many cases, the extent of demulsification of the water/oil emulsions was greater with sodium bicarbonate than that with sodium chloride or sodium carbonate.

The stability of the emulsions increased as the pH increased indicating that sodium bicarbonate reduces the formation of stable emulsions.

The stability of the emulsions also increased with salinity. In most cases, the 1 percent solution of sodium bicarbonate was effective in causing demulsification.

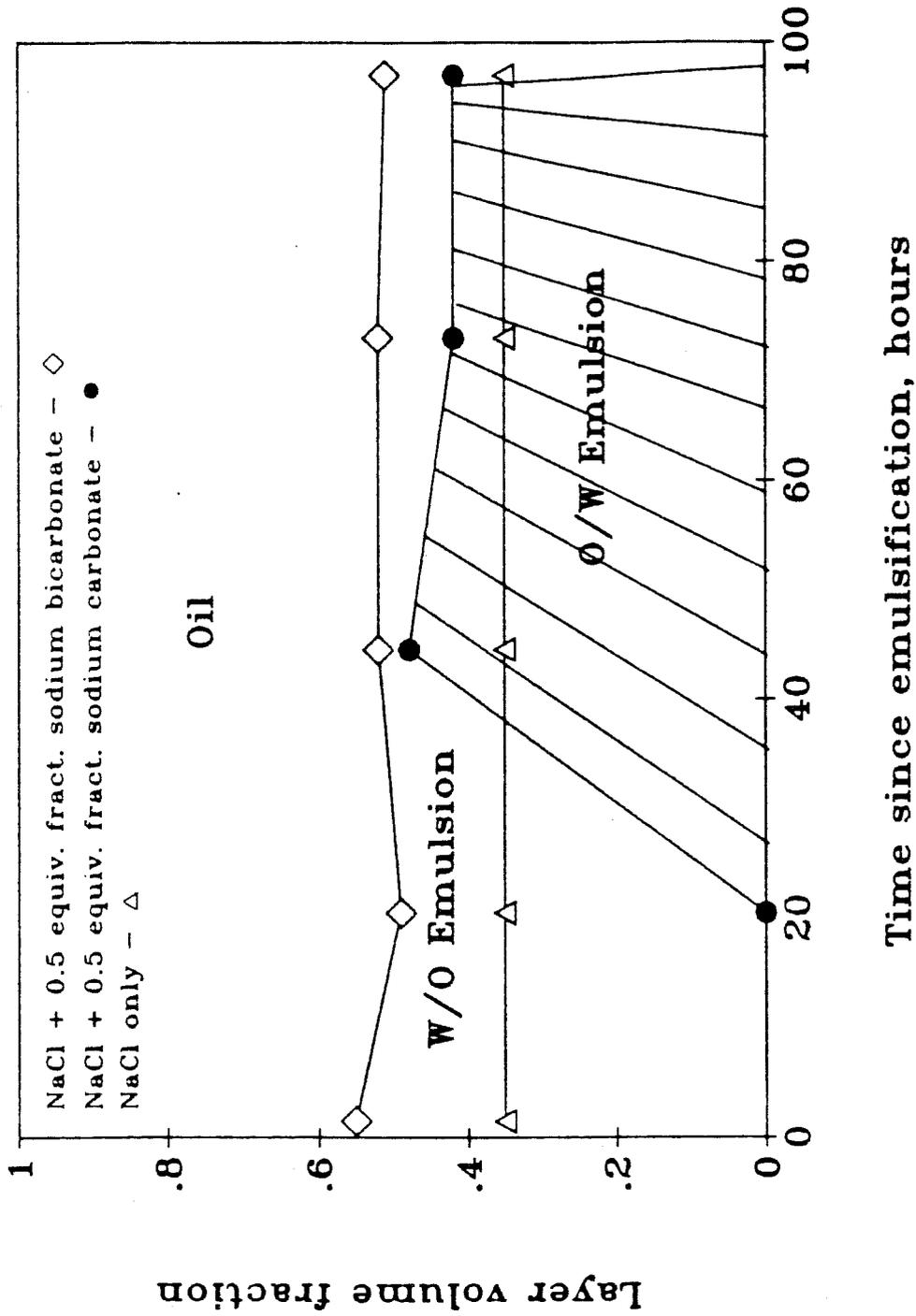


FIGURE 1a. - Demulsification of Wilmington crude #77032 in brines (171 meq/liter).
Emulsions formed at 78 F.

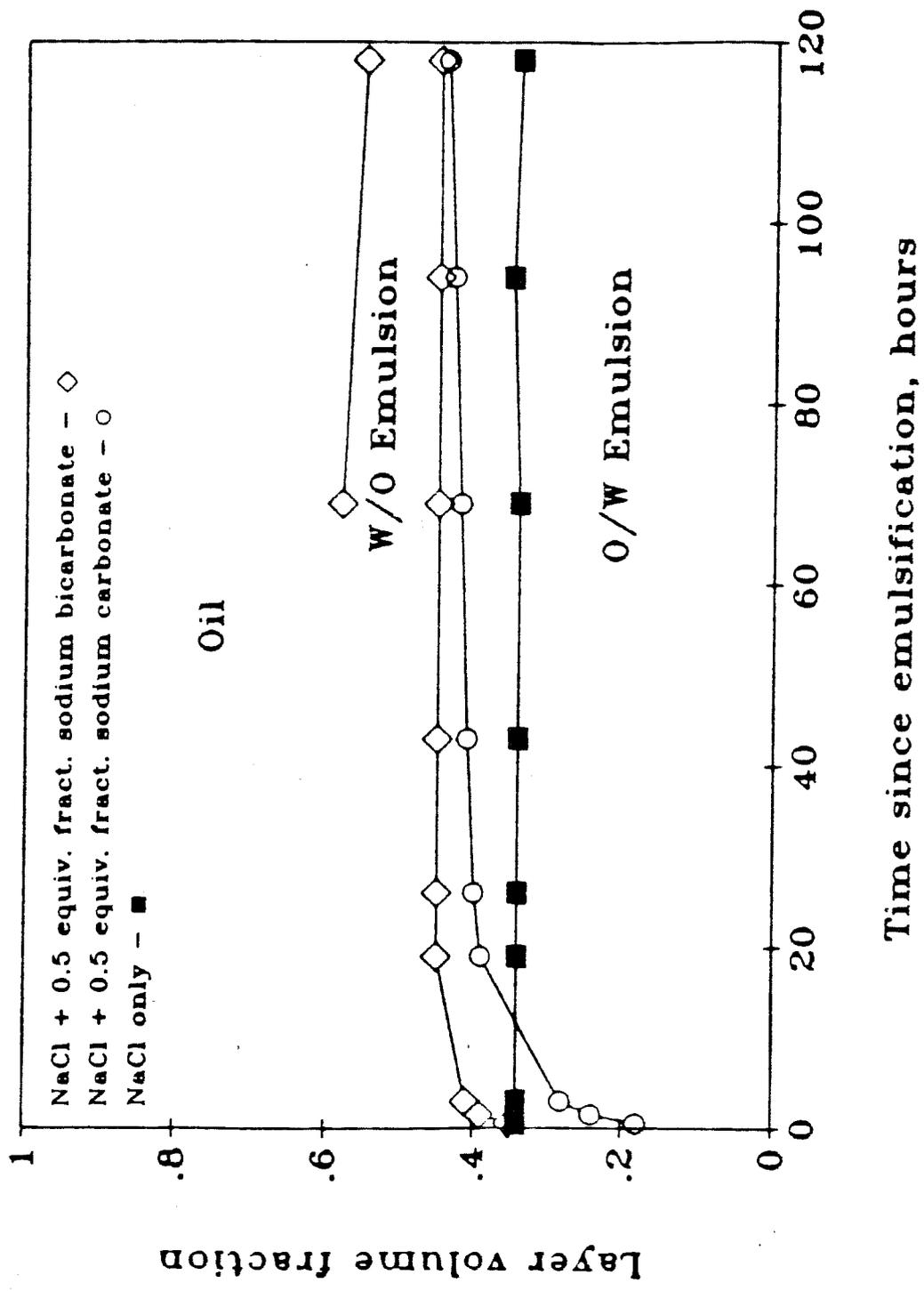


FIGURE 2a. - Demulsification of Midway-Sunset crude in brines (86 meq/liter).
 Emulsions formed at 122 F.

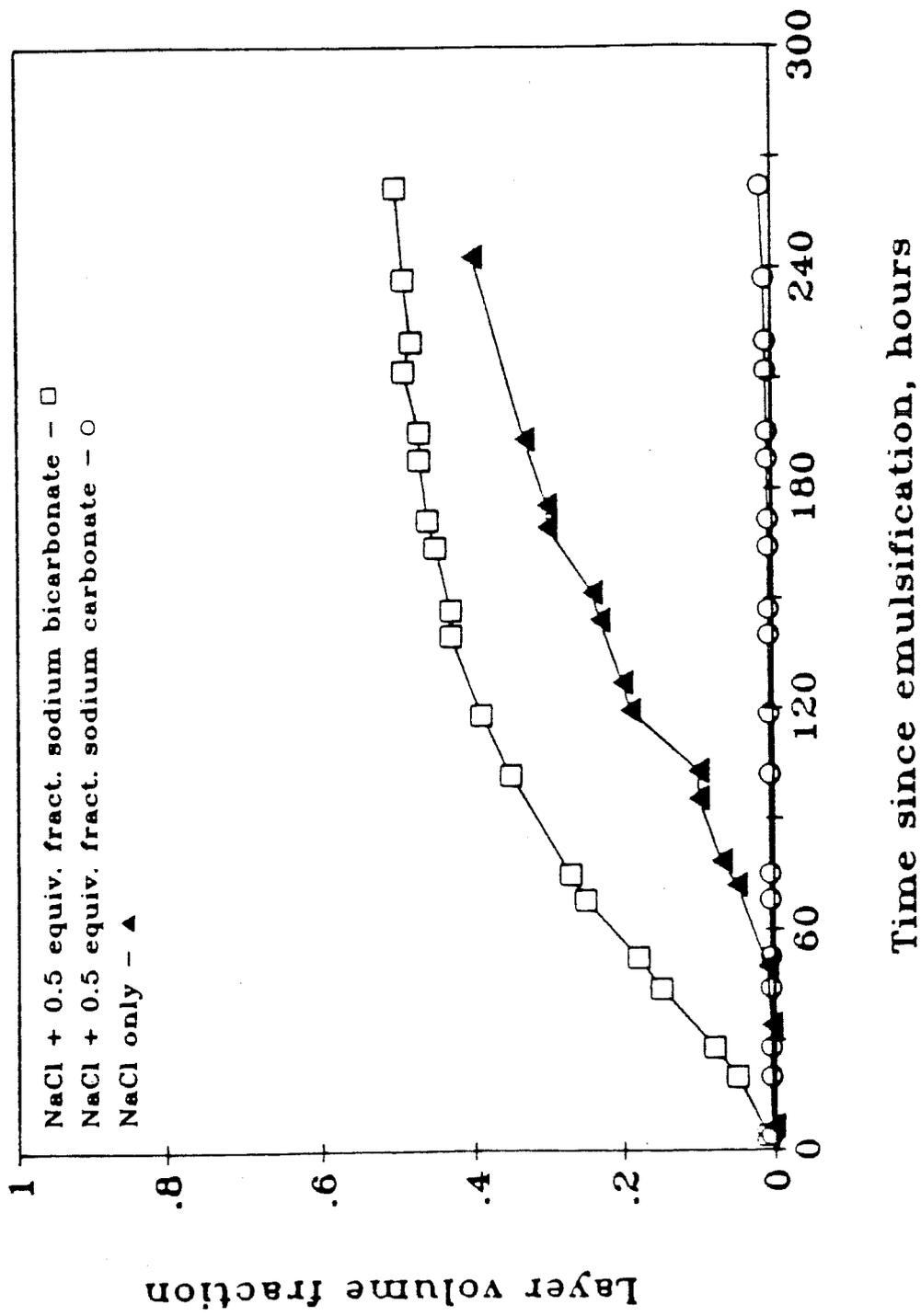


FIGURE 3a. - Demulsification of Noone crude diluted 1:2 with Delaware-Childers in brines (257 meq/liter). Emulsions formed at 78 F.

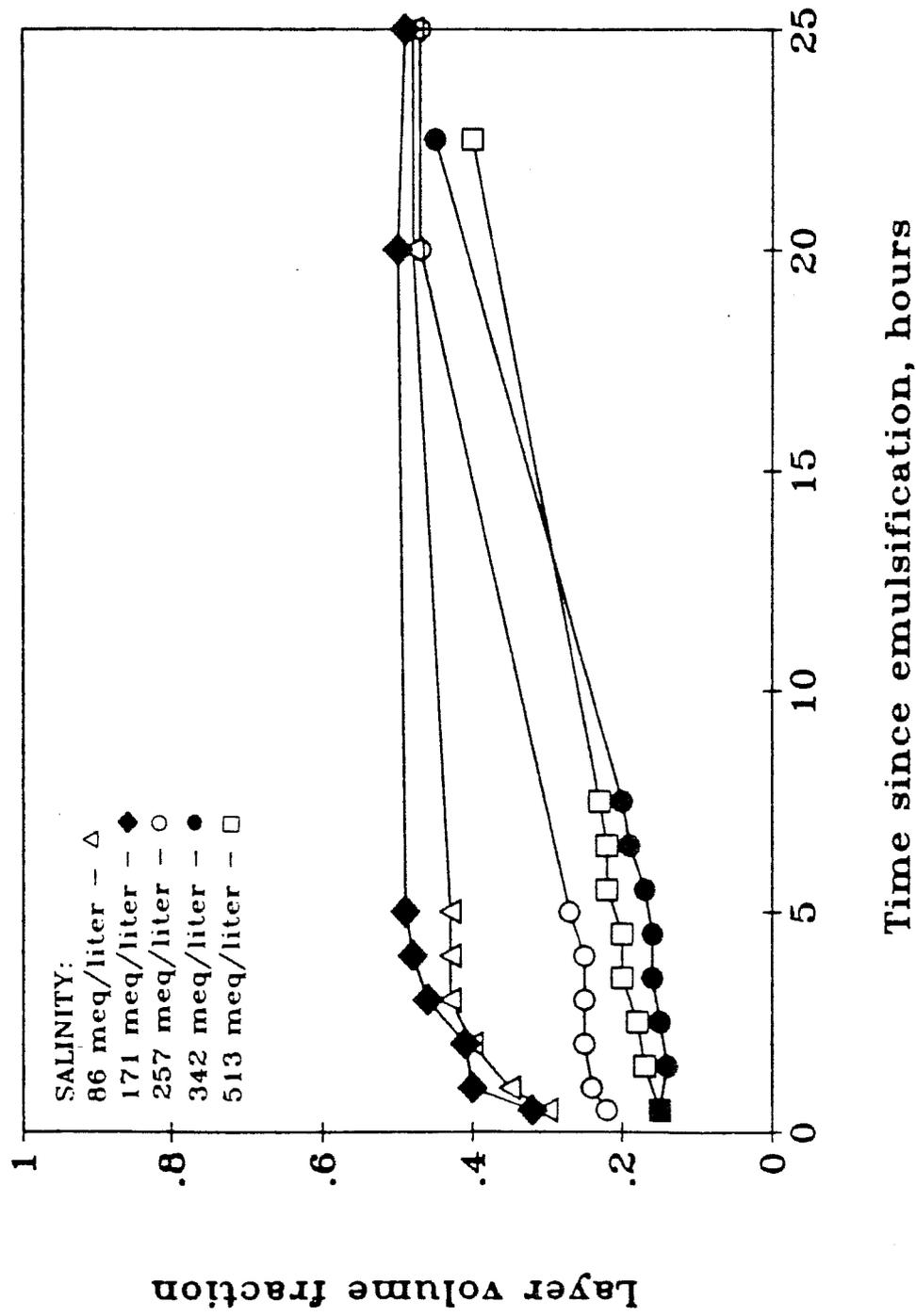


FIGURE 4a. - Demulsification of Wilmington 5G crude diluted 1:2 with Delaware-Childers in brines of (NaCl + 0.5 equivalent fraction NaHCO₃).

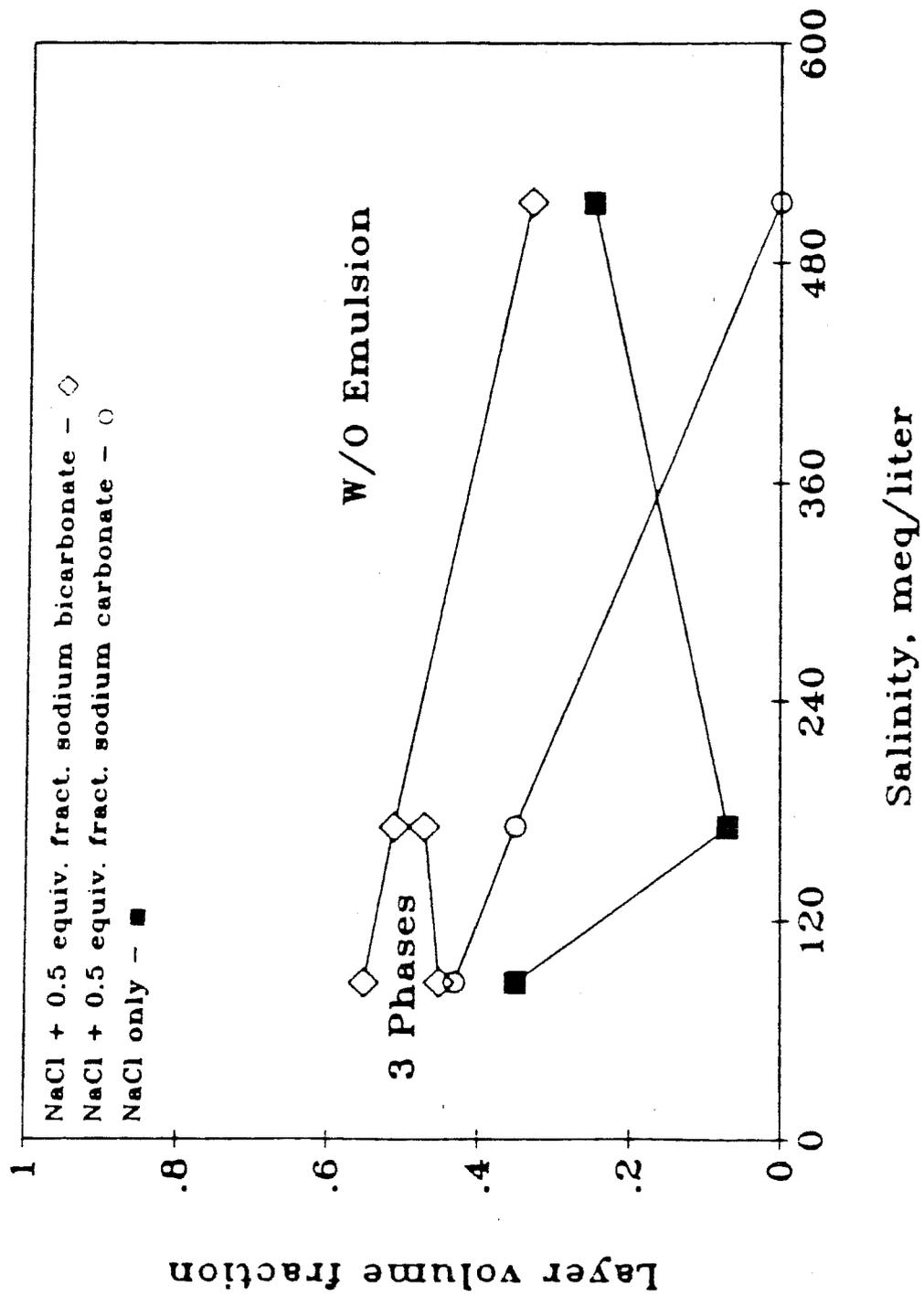


FIGURE 5a. - Demulsification of Midway-Sunset crude at 100 hours after emulsification.

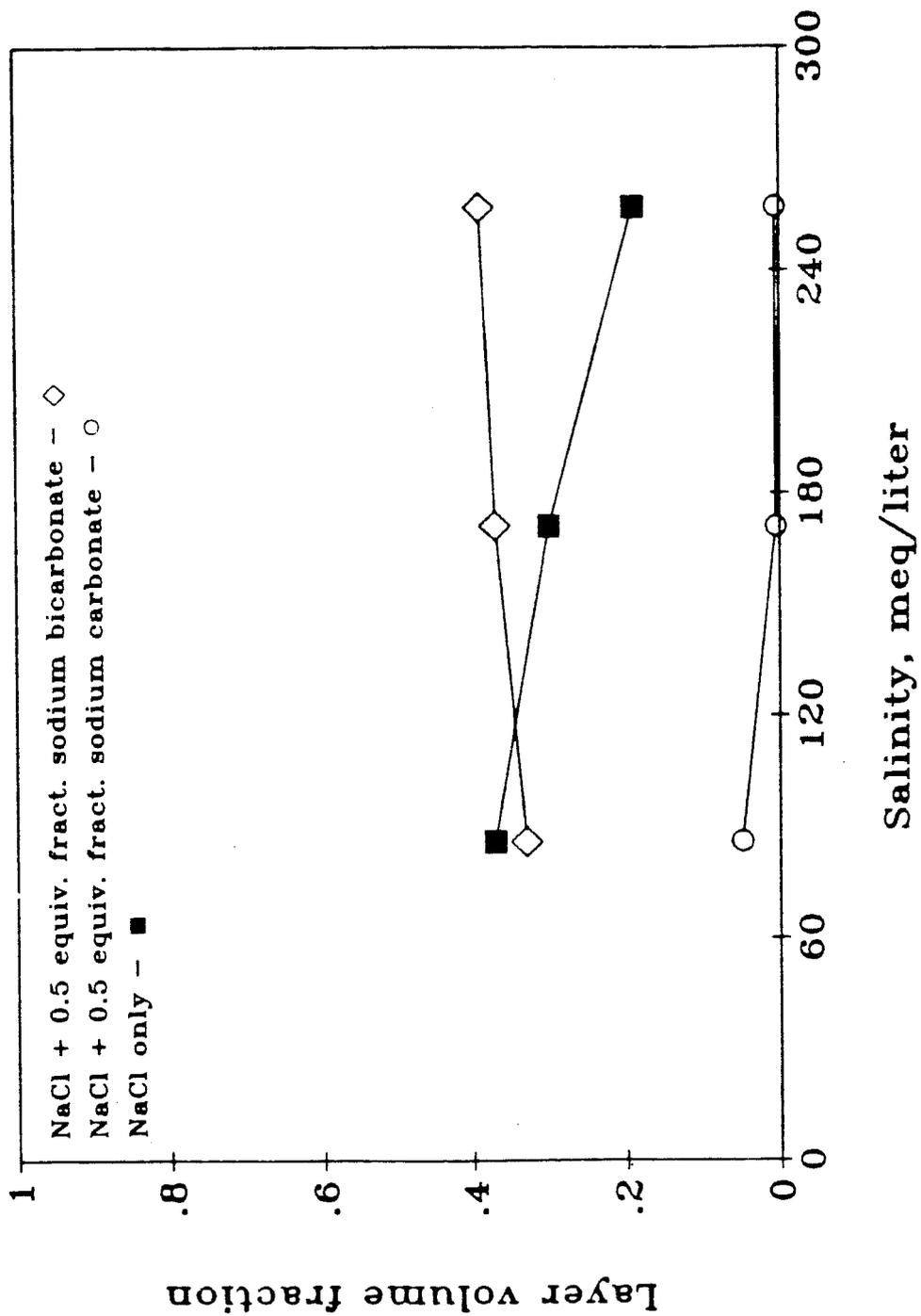


FIGURE 6a. - Demulsification of Noone crude diluted 1:2 with Delaware-Childers oil at 120 hours after emulsification.

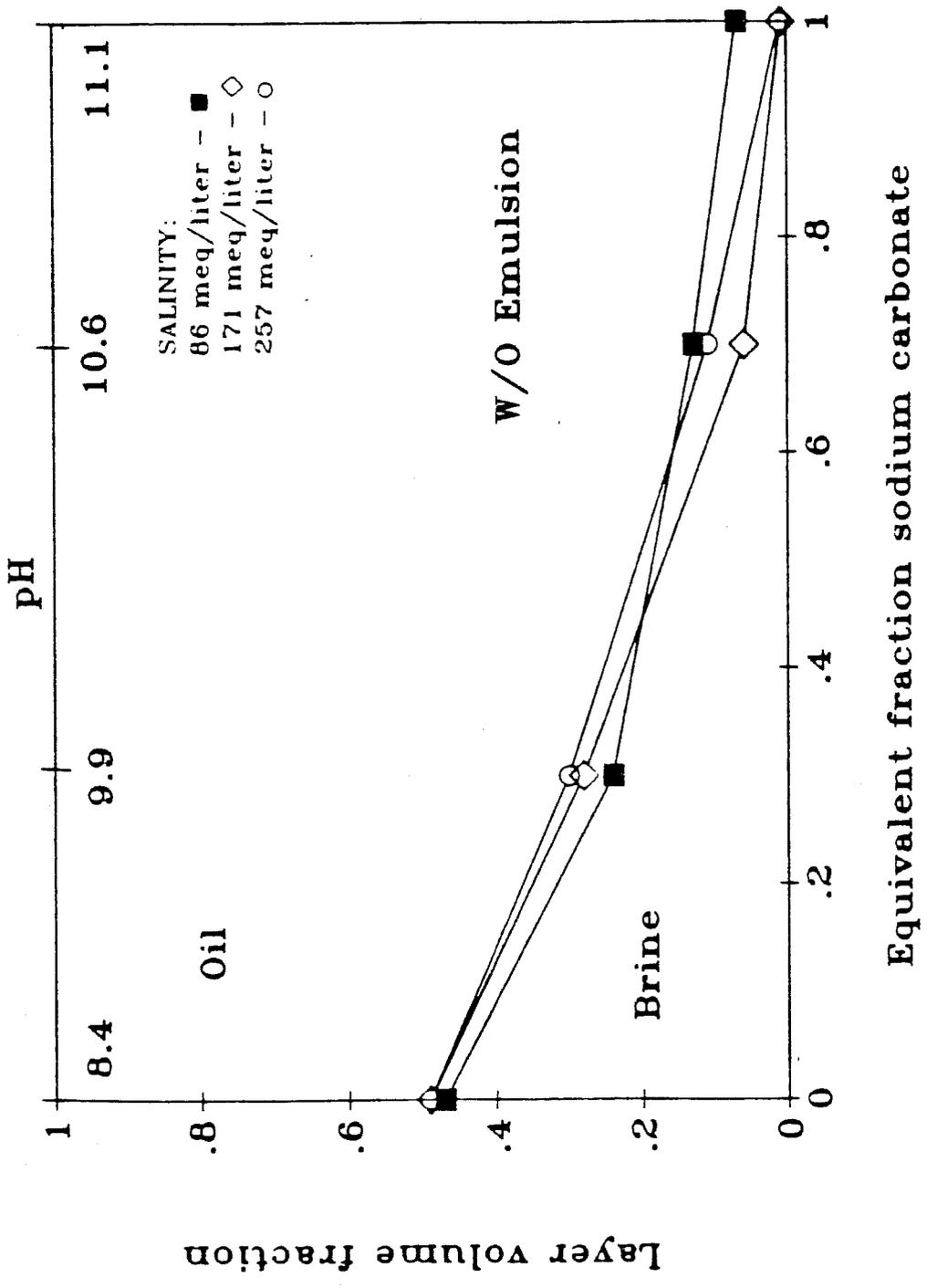


FIGURE 7a. - Demulsification of Noone crude diluted 1:2 with Delaware-Childers in mixtures of NaHCO₃ and Na₂CO₃ at 237 hours after emulsification.

SECTION B

This section concludes the experimentation on Task 1, which was to screen various oils for emulsion stability. The results on all the oils tested are tabulated in Table 2b according to increasing acid number. Also a separate table (3b) exists for Cerro-Negro and Cat-Canyon diluted with pure hydrocarbons.

Task 2 is the determination of the wetting properties of the cores in the presence of sodium bicarbonate compared with sodium chloride. A preliminary set of results is reported in table 4b.

Task 3 deals with coreflooding using sodium bicarbonate as the tertiary chemical slug. Table 5b reports the results on the first coreflood.

Experimental

Materials

Two additional oils were tested for emulsification behavior in test tubes: Cat-Canyon (Bureau of Mines #77069, Los Alamos, Calif.), 10.0° API; and Cerro-Negro (Bureau of Mines #80013, Venezuela), 8.2° API. Results from the Bureau of Mines analysis are given in table 1b.

Berea sandstone, about 400 md after firing at 800° F, was used for flood tests.

Wettability measurements were done using Berea sandstone, about 400 md not fired.

Procedures

Wettabilities were evaluated from capillary pressure data measured in the centrifuge, using the "Bureau of Mines" method (2). In the centrifuge, capillary pressures are proportional to the difference between water density and oil density, so with heavy oils, density nearly equal to water, only a fraction of the usual span of capillary pressures could be achieved at practical rates of rotation.

Dilution of oils with tetralin (tetrahydronaphthalene) was used to reduce viscosity, with minimal impact on the colloidal properties of the heavy ends. Dilution with toluene was used to reduce density.

TABLE 1b. - Properties of crude oils

Oil	Gravity, 60° F		S	N	C Res.	Acid Number	Residue*
	Spec. g/cm ³	API deg					
Cat Canyon B77069	1.000	10.0	6.98	0.746	-	0.92	69.8
Cerro-Negro B80013	1.013	8.2	3.85	0.170	27.7	3.27	66.4

*Temperature >572° F; Pressure = 40 mmHg.

For flood tests, ten-inch long cores, 1½-inch in diameter, were saturated with brine under vacuum, and flooded with oil at a high rate to a residual brine saturation. Waterfloods and bicarbonate floods were performed at 4.85 ft./da., and 75° F. Total brine concentration in meq/L was kept constant throughout. For NaCl alone, 171 meq/L is one percent, or 10,000 ppm. Bicarbonate slugs were 50 equivalent percent NaHCO₃ and 50 percent NaCl.

Experimental Results

Emulsion Studies

Figures 1b and 2b present the behavior of Cat-Canyon and Cerro-Negro oils at selected salinities. The very slow rate of demulsification is partly associated with the low buoyancy of these heavy oils. Results for all oils tested on the project are shown in tables 2b and 3b. It can be seen that there is no significant correlation between the effect of bicarbonate (or carbonate) with the acid number. Although alkaline agents theoretically work best on crude oils with high acid number, these oils have the tendency to be lower in API gravity. Thus, there is a trade off between the effectiveness of alkaline agents and the slow rate of demulsification caused by the low buoyancy of these acidic crude oils. Furthermore, Cerro-Negro is a fairly acidic oil, but demulsification was much slower with NaHCO₃ than with NaCl

brines. On the other hand, for the Noone, Cat-Canyon, Wilmington 5G, and Midway-Sunset oils, bicarbonate at 171 meq/L was distinctly superior for demulsification as compared with NaCl or Na₂CO₃.

Wettability

The average wettability number measured with Wilmington 5G and brine (1% and 3% NaCl) was found to be 0.41 ± 0.05 , which indicates a fairly water-wet condition. For an oil-wet system, Cerro-Negro (diluted 1:1 with tetralin) was selected because it appeared to wet the walls of glass test tubes. The scatter of the results in table 4b is the result of being restricted to small volumes of displaced fluid (<0.7 cc). The maximum capillary pressure was 2.2 psi, about 28 percent of the standard used in reference 2. Nevertheless, it is reasonable to conclude that the natural tendency of Cerro-Negro to wet the solid is largely counteracted by bicarbonate.

Flood tests

Oil recovery by injection of bicarbonate was tested on Wilmington 5G diluted 1:2 with Delaware-Childers, a system that underwent fairly prompt demulsification in test tubes. Two tests were run with brines of total concentration 171 meq/L. The results are shown in table 5b. Test #1 used bicarbonate as a tertiary agent after waterflooding, which recovered 7.3 percent of the waterflood residual oil. Test #2 used bicarbonate from the beginning of water injection. The difference in total oil recovery between the two runs is within the variation expected for flood tests. A preliminary set of measurements of interfacial tension (using the spinning drop technique) indicated that tension at the Wilmington oil/brine interface was not significantly reduced by bicarbonate.

Discussion

Two additional heavy oils were tested for emulsification behavior with sodium bicarbonate. A review of all the results indicates that sodium bicarbonate, in most cases, is more effective in causing coalescence of oil droplets. Subsequently, the emulsions break and the formation of oil banks can occur in flood processes.

Preliminary work has begun to correlate these results with acid number and asphaltene content. It appears that the crude oils that work best with bicarbonate have acid numbers below 1 mg KOH/g. This is true for oils diluted with either Delaware-Childers or pure hydrocarbon. Also, these oils have a high content of asphaltenes. However, more experimental work needs to be done to confirm this correlation.

Conclusions

In one coreflood test, using Wilmington 5G crude oil, the sodium bicarbonate chemical slug recovered 7.3 percent of the residual oil after waterflooding. Due to the absence of interfacial-tension reduction or wettability reversal with Wilmington 5G, its interaction with bicarbonate is limited to emulsification/demulsification effects.

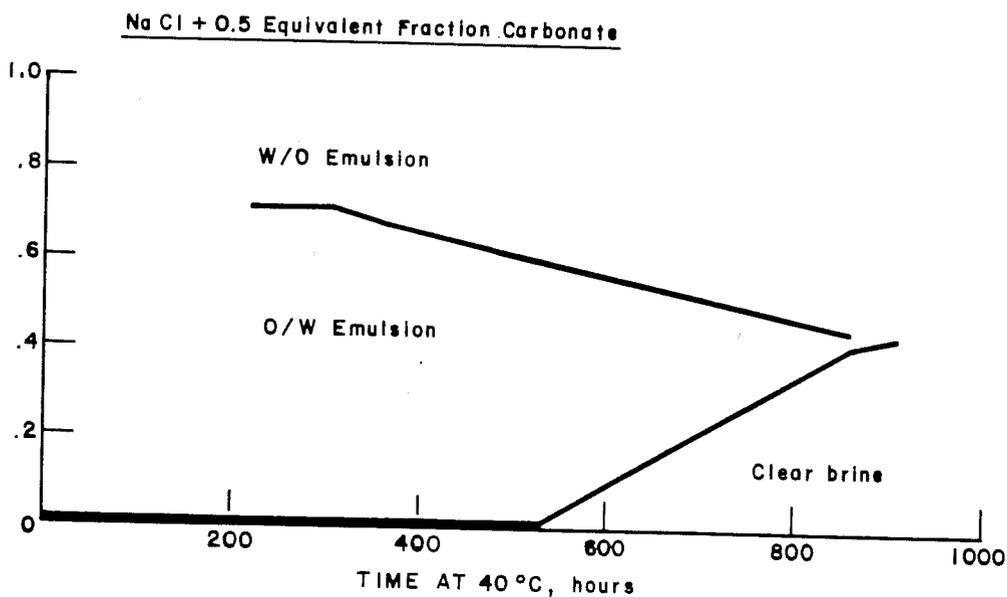
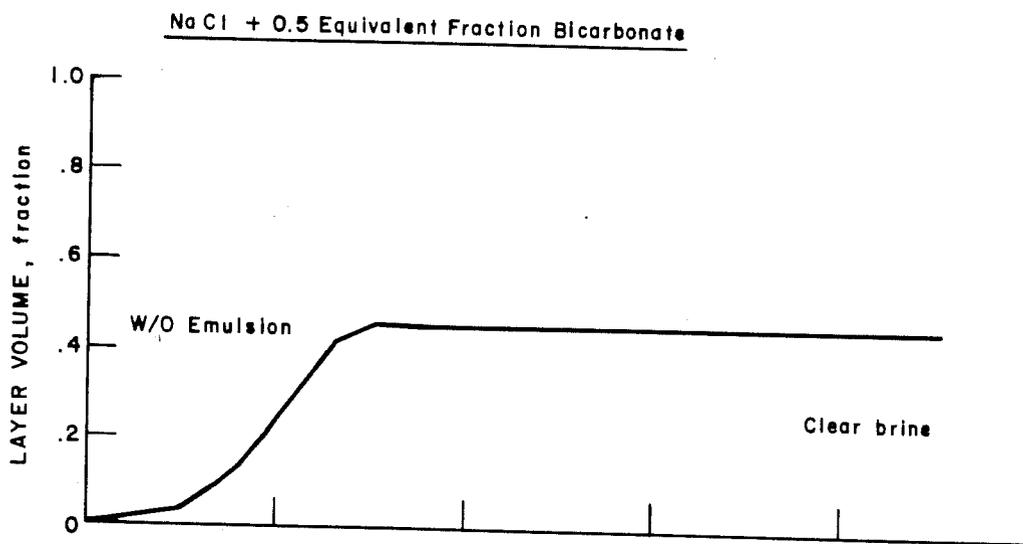
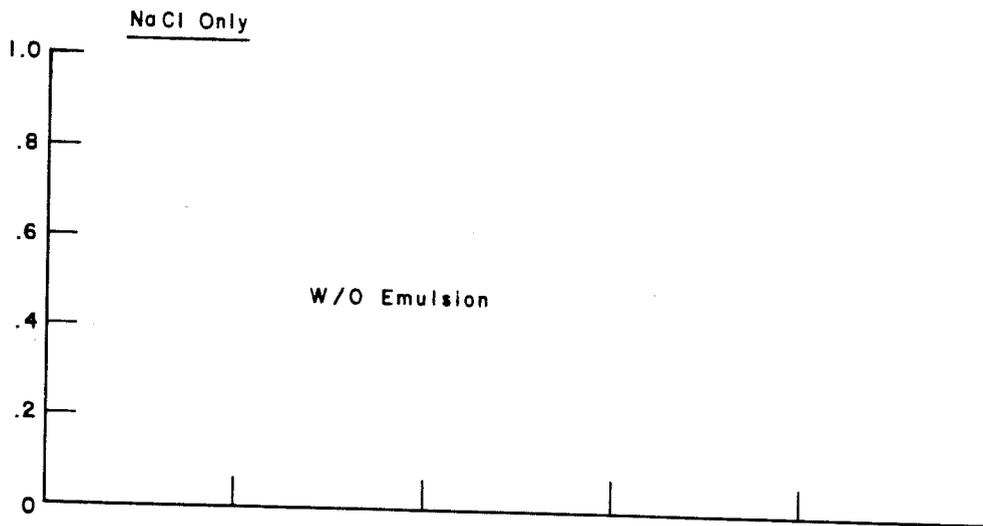


FIGURE 1b. - Demulsification of Cat-Canyon crude oil #77069 diluted 1:2 with Delaware-Childers oil, in brines at 171 meq/liter.

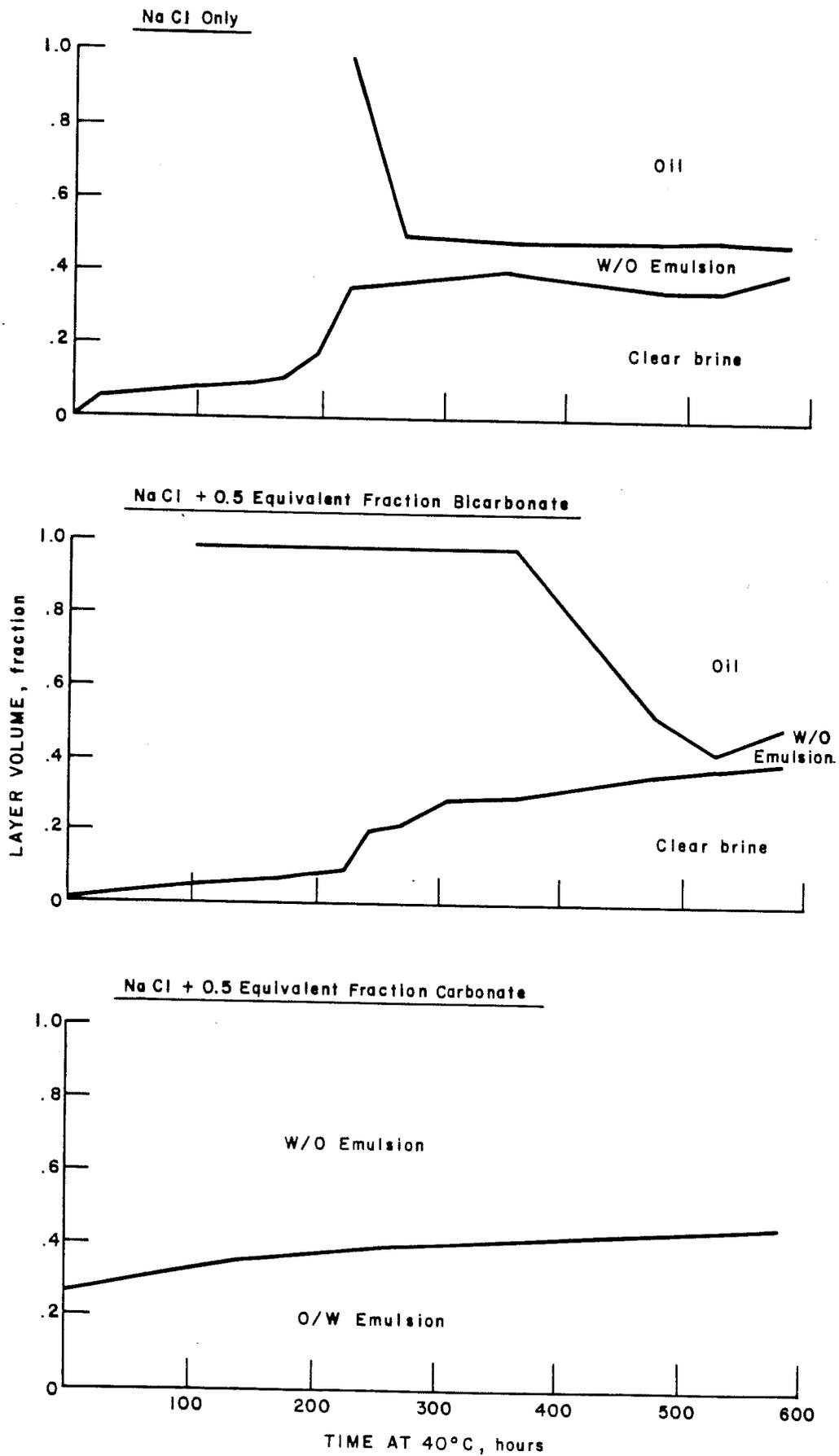


FIGURE 2b. - Demulsification of Cerro-Negro crude oil #80013 diluted 1:2 with Delaware-Childers oil, in brines at 86 meq/liter.

TABLE 2b. - Demulsification tests with various crude oils (25° unless otherwise stated)

Oil	Hours after Emulsification	After-dilution value of density ^c acid no.	Effect of Brine on Water Breakout														
			NaCl		NaHCO ₃		Na ₂ CO ₃										
			86	171	513	86	171	513	86	171	513						
Total meq/L																	
Delaware-Childers	47	0.85	0.13	hc *	hc **	hc **	-	cb ***	cb ***	hc ****	-	cb ***	cb ***	cb ***	-	cb ***	cb ***
Noone ^a B80002	194	(0.88)	0.18	cb ***	cb **	-	cb **	cb ***	cb ***	-	cb ***	0	0	0	-	0	-
Cat Canyon ^a B77069	860 ^b	(0.90)	0.40	0	0	0	0	cb ***	cb ***	cb **	cb **	o/w **	o/w **	cb **	cb **	cb **	cb **
Wilmington 5G ^a	25	0.88	0.77	-	hc ***	hc ***	cl ***	cl ***	cb ***	cb **	cb **	o/w ***	o/w ***	cl **	cl **	cb **	cb **
Cerro Negro ^a B80013	359 ^b	0.90	1.18	hc **	hc **	hc **	hc **	hc **	0	0	0	o/w **	o/w **	cb *	cb *	0	0
Wilmington B77032	97	0.97	2.31	cb **	cb **	cb **	cl ***	cl ***	cl ***	cb *	cb *	o/w *	o/w **	o/w **	0	0	0
Midway-Sunset B77067	118	0.97	4.15	cb **	0	cb **	cl **	cl **	cl ***	o/w **	o/w **	o/w **	o/w **	o/w **	0	0	0

^a - diluted 1:2 with Delaware-Childers oil

^b - time at 40° C

^c - values in parentheses are linearly interpolated

Symbols

0 - < 0.063 Layer vol. Fraction

* - 0.064-0.24

** - 0.25-0.45

*** - 0.46-0.50

- - did not determine

**** - >0.50

Description

cb - Clear brine
 cl - Cloudy brine
 o/w - oil in water emulsion
 hc - honeycomb appearance, a water in oil emulsion in suspension with clear brine

TABLE 3b. - Demulsification tests with various crude oils

Oil	Hours after Emulsification	Layer vol. Fraction	After-dilution value of density ^d acid no.		Effect of Brine on Water Breakout						
			86	171	NaCl	86	171	NaHCO ₃	86	171	Na ₂ CO ₃
Total meq/L			86	171	NaCl	86	171	NaHCO ₃	86	171	Na ₂ CO ₃
Cat Canyon ^b B77069	359	(0.93)	hc *	hc *	hc **	hc **	hc *	hc *	hc **	hc **	hc *
Cat Canyon ^a B77069	317	0.99	0	cb *	cb *	cl **	cb **	cb **	o/w **	ab **	ab ***
Cerro Negro ^c B80013	286	(0.92)	cb ***	cb ***	cb ***	cb ***	cb ***	cb ***	cl **	o/w ***	o/w ***
Cerro Negro ^a B80013	480	1.0	-	cb **	cb **	-	cb **	cb **	-	ab **	0
Cerro Negro ^a B80013	505	1.0	cb **	-	-	cb **	-	-	cb **	ab ***	-

Symbols

0 - < 0.063 Layer vol. Fraction
 * - 0.064-0.24
 ** - 0.25-0.45
 *** - 0.46-0.50
 **** - >0.5
 - - did not determine

Diluent

a - tetralin 1:1
 b - toluene 1:1
 c - toluene 1:2
 d - values in parentheses are linearly interpolated

Description

ab - amber brine
 cb - clear brine
 cl - cloudy brine
 o/w - oil in water emulsion
 hc - honeycomb appearance, a water in oil emulsion in suspension with clear brine

TABLE 4b. - Wettability numbers
(duplicate runs)

Wilmington 5G undiluted

1% NaCl	=	0.408
	=	0.378
3% NaCl	=	0.377
	=	0.477

Cerro-Negro #80013 diluted 1:1 with Tetralin

3% NaCl	=	-1.267
	=	-0.534
3% NaHCO ₃	=	0.053
	=	-0.317

TABLE 5b. - Oil recovery of Wilmington 5G crude oil by a
sodium bicarbonate coreflood

	<u>Test 1</u>	<u>Test 2</u>
S_{oi} at beginning of waterflood	77.8%	74.9%
S_{orw} at end of waterflood	40.6%	-
S_{orc} at end of bicarbonate flood	38.0%	40.2%
Recovery (% Pore Volume)	3.0%	-
Recovery (% of S_{orw})	7.3%	-

SECTION C

This final section includes:

- o An update on additional experimental results.
- o A discussion of what the project has shown about the potential marketability of sodium bicarbonate for enhanced oil recovery.
- o Comments on the pros and cons of other techniques for utilizing sodium bicarbonate.
- o Specific recommendations for further research.

Experimental Results

Screening Tests

Figures 1 through 6 present the visual results of the screening tests on Cat-Canyon and Cerro-Negro crude oils. It can be seen that Cat-Canyon had good emulsification/demulsification properties, and Cerro-Negro showed signs of wettability reversal upon the addition of sodium bicarbonate.

Because of time limitations, further experiments were limited to tests using Cerro-Negro crude. It was tested quantitatively for wettability effects and was used in coreflooding experiments.

Wettability

Because of the high uncertainty of wettability numbers for heavy oils when measured by the "Bureau of Mines" method, recent measurements were made by the Amott-Harvey method (3), which entails much higher centrifugal forces, or by a simple imbibition test that measures volumes rather than weights. The results in table 1c verify that Cerro-Negro crude undergoes a distinct wettability change on going from a chloride system to a bicarbonate system. This was observed with the crude diluted with either Delaware-Childers or tetralin. The results in table 1c show a change opposite to that inferred from the uncertain results of the Bureau of Mines method. As before, the Wilmington oil (diluted with Delaware Childers) was preferentially water-wet and was not strongly affected by sodium bicarbonate.

Flood Tests

Table 2c presents the results of oil-recovery coreflood tests on Cerro-Negro diluted with tetralin. Also shown for comparison are the results on Wilmington presented previously. Judging by this very limited number of results, the tertiary recovery was larger with Cerro-Negro, for which there was a wettability change, than with Wilmington, for which there was a more rapid coalescence of emulsions, on adding sodium bicarbonate. It should be pointed out that in the tests on Cerro-Negro the slug of sodium bicarbonate solution was smaller, but a polymer slug was used for mobility control.

Discussion

The sodium bicarbonate chemical slug recovered 7.3 percent (Wilmington crude) and 13.2 percent (Cerro-Negro crude) of the residual oil after waterflooding. The oil recovered is probably associated more with a change in wetting of the core than with oil bank formation (emulsification/-demulsification). It is likely that this is the basis for the use of bicarbonates in releasing bituminous material from tar sands (4). Thus, our results hold promise that sodium bicarbonate could have a significant market as an agent for enhanced oil recovery. In the cases examined, the amount of oil produced was not large. Production could probably be increased by optimizing the formulation of the sodium bicarbonate solution. This would be accomplished by adjustments in the salinity, and perhaps by adding some polymer and/or surfactant. Both these adjustments would have to be matched to the properties of the target oil.

Conclusions

The most significant finding of this study is that sodium bicarbonate is capable of producing tertiary oil in laboratory coreflood tests.

The observed tertiary recovery is associated more with a wettability change (Cerro-Negro crude) than with emulsification/demulsification behavior (Wilmington crude).

Other Potential Applications

Our proposal suggested four items for further consideration:

1. Sodium bicarbonate might be used in combination with other EOR chemicals. The use of the strong alkaline agents with surfactants has been investigated at several laboratories. In the work of Nelson et al. (5), the observed results were associated with the generation of surfactants from the acid constituents of the crude oil. Bicarbonate is believed to work by altering the properties of asphaltene films at the liquid and solid interface. This effect in connection with the reduction of interfacial tension by surfactants could lead to enhanced mobilization of oil. Strong alkaline agents also show synergistic interactions with surfactants and polymers (6). If a similar synergism occurs with sodium bicarbonate, it would be longer lasting, because the bicarbonate is not expected to be consumed by reaction with reservoir rock.
2. It is desirable to verify that sodium bicarbonate is nonreactive with reservoir minerals. A particular advantage would be for reservoirs with soluble or exchangeable calcium, which precipitates hydroxide, silicates, or carbonate in the conventional agents. If it is demonstrated that sodium bicarbonate is comparable to the conventional alkaline agents in mobilizing certain oils, it would be a strong selling point that it also surpasses the others in not being lost by reaction with the reservoir rock.
3. The use of sodium bicarbonate as a preflush is not promising, because a systematic study (7) has indicated that other alkaline or buffering agents do not compete with simple NaCl brine in cost and effectiveness.
4. Injection of sodium bicarbonate followed by steam to release CO₂ in situ is possibly worth some investigation, but this is not recommended at this time. The equilibrium pressure of CO₂ over solid sodium bicarbonate is 2.6 atmospheres at 250^o F. This is too low to be effective unless solubility relations in water and oil are unexpectedly favorable.

Recommendations

1. It is recommended that the preliminary conclusions be verified by extending coreflood tests to other wetting oils.
2. More attention should be paid to mobility control; that is, the benefit of "thickening" the sodium bicarbonate solution so it does not finger through the oil bank.
3. In the same tests, the effluent should be analyzed to check on loss of bicarbonate on passing through the core.
4. If these results are favorable, recoveries should be measured using oilfield cores.
5. Comparison should be made with the performance of the other alkaline agents.
6. Exploratory measurements should be made of the oil-recovery potential of a combined slug of sodium bicarbonate plus surfactant.

References

1. Strassner, J. E. Effect of pH on Interfacial Films and Stability of Crude Oil-Water Emulsions. March, 1968, Journ. of Pet. Tech., pp. 303-312.
2. Donaldson, E. C., R. D. Thomas, and P. B. Lorenz. Wettability Determination and its Effect on Recovery Efficiency. Soc. Pet. Eng. Journ., Mar., 1969, pp. 13-20.
3. Boneau, D. F. and R. L. Clampitt. A Surfactant System for the Oil-Wet Sandstone of the North Burbank Unit. SPE 5820, presented at the Improved Oil Recovery Symposium, Tulsa, OK, March 22-24, 1976.
4. Globus, A. R. Process for the Recovery of Bituminous Material from Tar Sands. U. S. Patent 4,120,777 (1978).
5. Nelson, R. C., J. B. Lawson, D. R. Thigpen, and G. L. Stegemeier. Cosurfactant-Enhanced Alkaline Flooding. SPE/DOE 12672, presented at Fourth Symposium on Enhanced Oil Recovery, Tulsa, OK, April 15-18, 1984.
6. Krumrine, P. H. and J. S. Falcone, Jr. Surfactant, Polymer, and Alkali Interactions in Chemical Flooding Processes, SPE 11778.
7. Surkalo, H. and G. Pouska. Experimental Evaluation of Reservoir Pretreatment in Chemical Flooding.. Final Report. U. S. Department of Energy DOE/BC/10027-12 (Feb., 1981).

TABLE 1c. - Improved data on the effect of sodium bicarbonate on wettability

Oil	Amott-Harvey		Bureau of Mines		Water imbibition ^a	
	wettability		wettability		(PV)	
	<u>NaCl</u>	<u>NaHCO₃*</u>	<u>NaCl</u>	<u>NaHCO₃*</u>	<u>NaCl</u>	<u>NaHCO₃*</u>
Cerro-Negro			(3%)	(3%)		
diluted 1:2 with			0.079	-0.030		
Delaware-Childers			0.076	-0.023		
Cerro-Negro					(3%)	(3%)
diluted 1:1 with					0.35	0.20
tetralin					0.30	0.26
Wilmington 5G	(1%)	(1%)				
diluted 1:2 with	0.61	0.77				
Delaware-Childers						

^a - Water imbibed by a core at irreducible S_w . No oil was imbibed by the same core at residual S_o .

() - values in parentheses are the percentage total salt concentration of brine.

* - sodium chloride + 0.5 equivalent fraction of sodium bicarbonate.

TABLE 2c. - Flood test results: oil recovered by injection of a slug with NaCl + 0.5 equivalent fractions sodium bicarbonate (5 ft/day)

Oil	Wilmington 5G diluted 1:2 with Delaware-Childers		Cerro-Negro diluted 1:1 with tetralin	
	(1%)	(1%)	(3%)	(3%)
Pore volumes sodium bicarbonate slug	4.9	5.6	2.0	2.1
Pore volumes polymer slug (47 cps NaIFlow 550)	0.0	0.0	1.1	1.0
<u>Oil Saturations</u>				
Initial (S_{oi})	0.78	0.75	0.80	0.78
Waterflood residual (S_{orw})	0.41	-- ^a	0.46	0.45
Chemical flood residual (S_{orc})	0.38	0.40	0.40	0.39
Recovery (% of S_{orw})	7.3%	--	13.0%	13.3%
Recovery (% Pore Volume)	3.0%	--	6.0%	6.0%

() - values in parentheses are the total salt concentration of brine.

a - no waterflood. Sodium bicarbonate was injected into core with irreducible water.

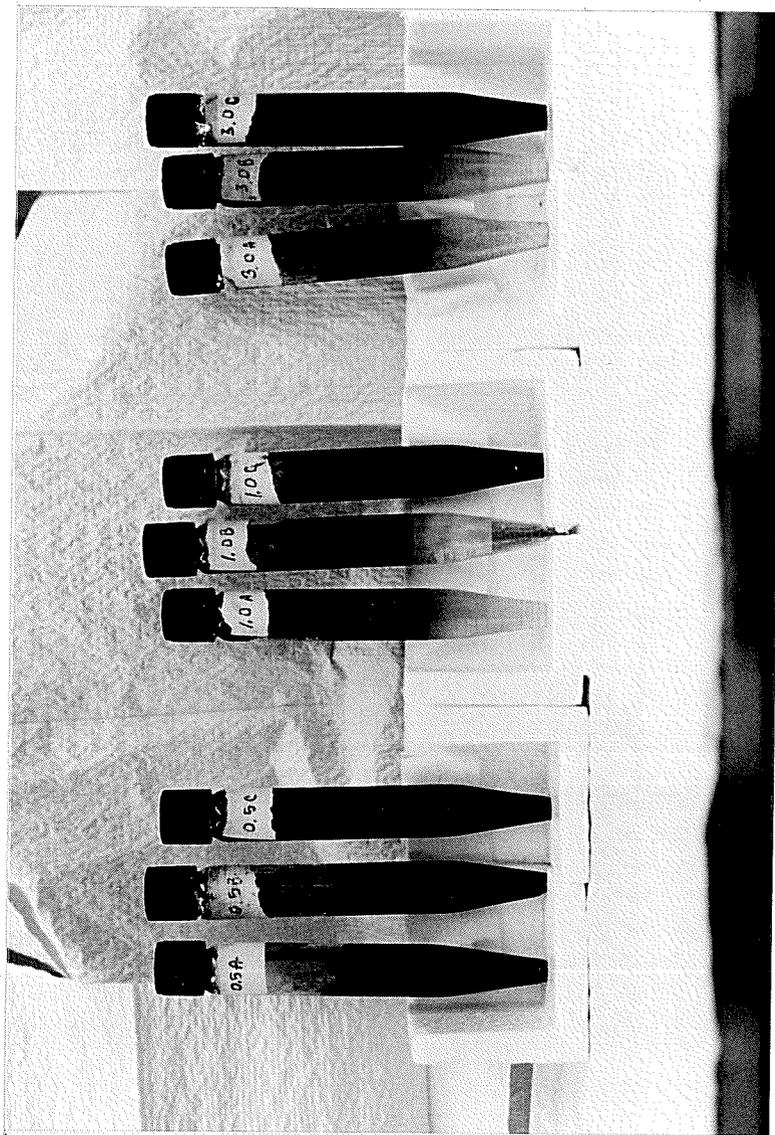


FIGURE 1. - Cat-Canyon diluted 1:2 with Delaware-Childers. Emulsification-Demulsification experiment at 3 salinities. From left to right, 86 meq/L, 171 meq/L, and 513 meq/L. Label A is NaCl + 0.5 equiv. fraction Na_2CO_3 , label B is NaCl + 0.5 equiv. fraction NaHCO_3 , and label C is NaCl only.

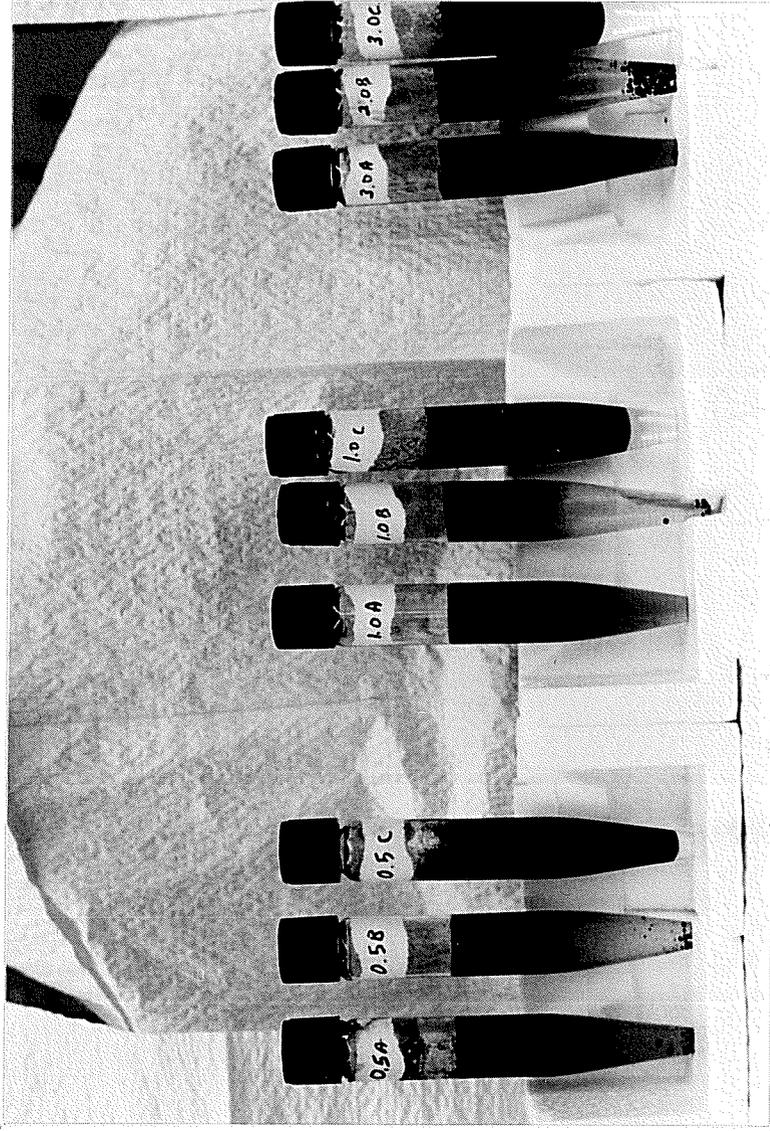


FIGURE 2. - Cat-Canyon diluted 1:1 with Tetralin. Emulsification-Demulsification experiment at 3 salinities. From left to right, 86 meq/L, 171 meq/L, and 513 meq/L. Label A is NaCl + 0.5 equiv. fraction Na_2CO_3 , label B is NaCl + 0.5 equiv. fraction NaHCO_3 , and label C is NaCl only.

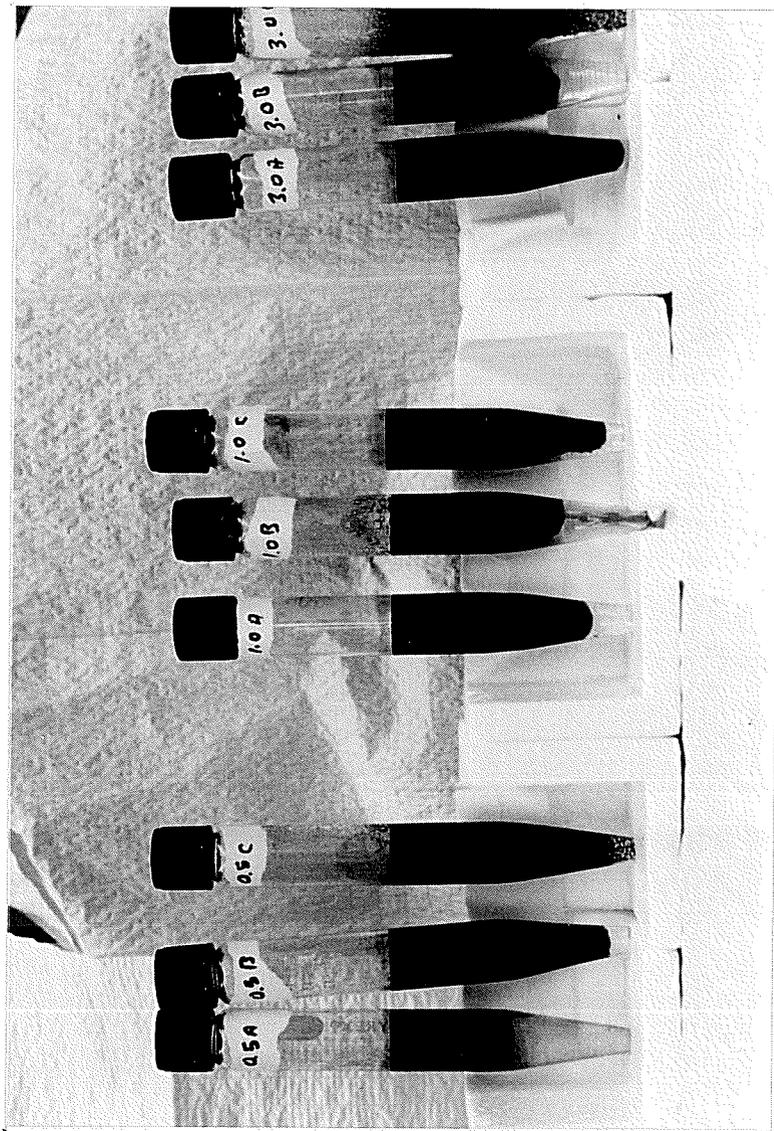


FIGURE 3. - Cat-Canyon diluted 1:1 with Toluene. Emulsification-Demuulsification experiment at 3 salinities. From left to right, 86 meq/L, 171 meq/L, and 513 meq/L. Label A is NaCl + 0.5 equiv. fraction Na_2CO_3 , label B is NaCl + 0.5 equiv. fraction NaHCO_3 , and label C is NaCl only.

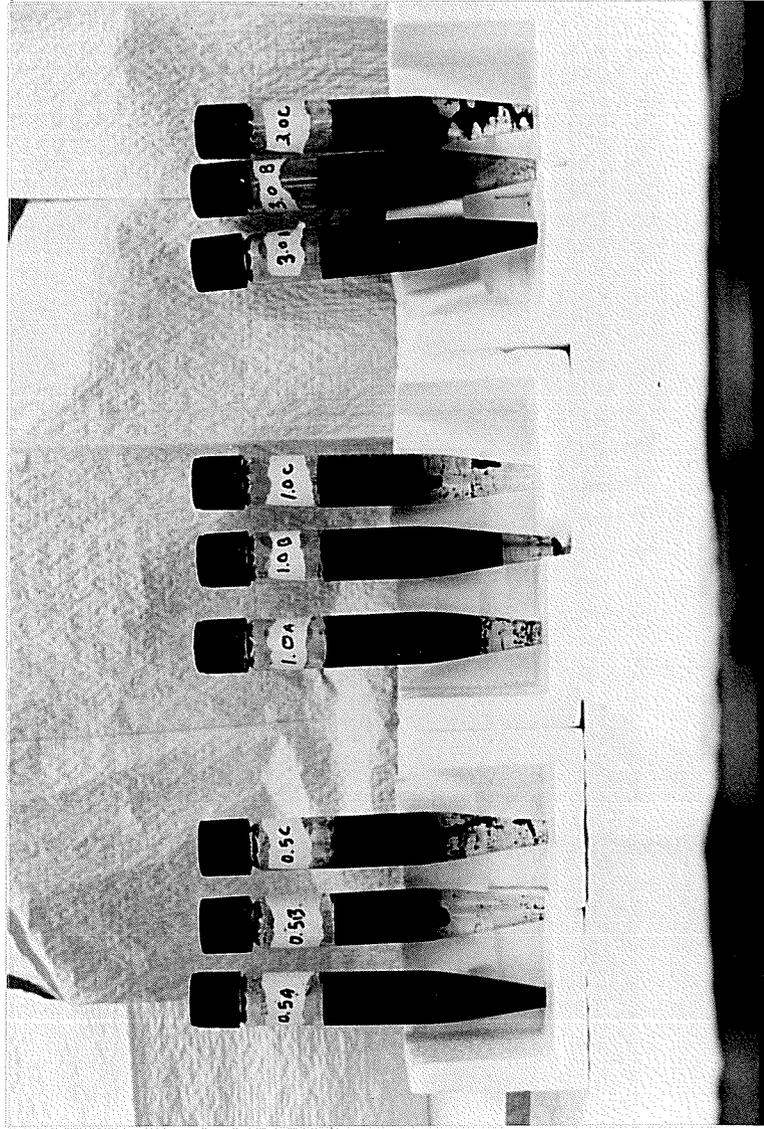


FIGURE 4. - Cerro-Negro diluted 1:2 with Delaware-Childers. Emulsification-Demulsification experiment at 3 salinities. From left to right, 86 meq/L, 171 meq/L, and 513 meq/L. Label A is NaCl + 0.5 equiv. fraction Na_2CO_3 , label B is NaCl + 0.5 equiv. fraction NaHCO_3 , and label C is NaCl only.

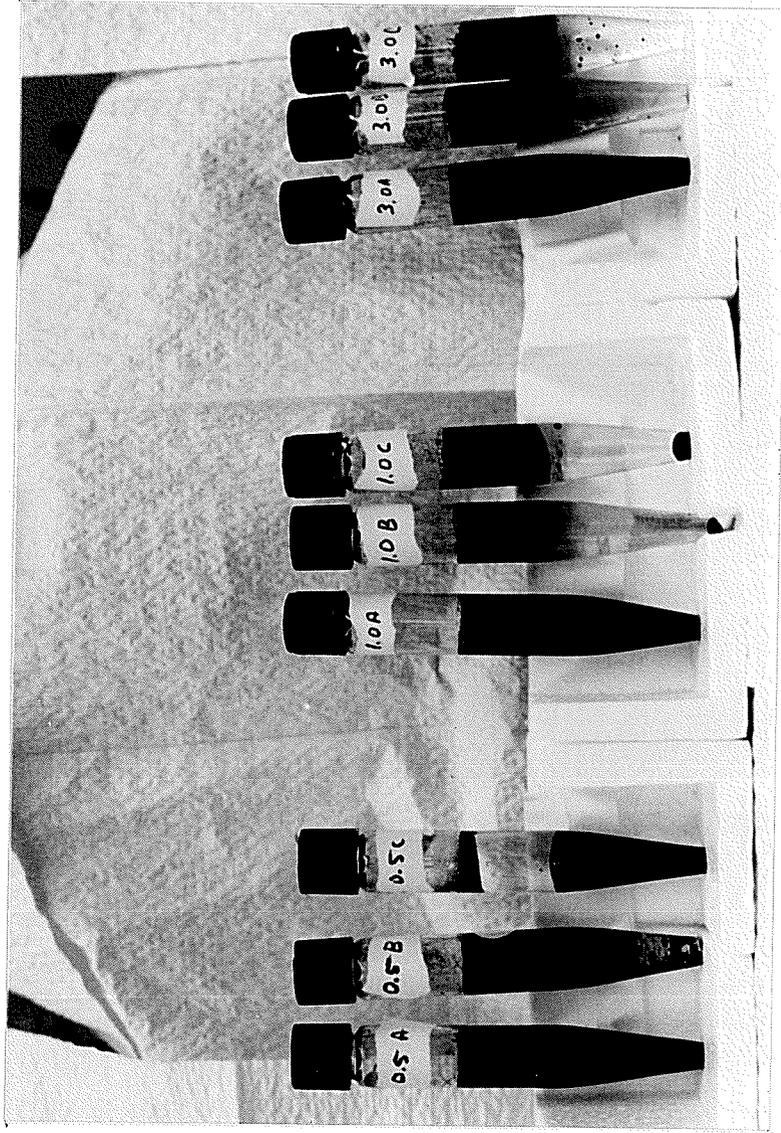


FIGURE 5. - Cerro-Negro diluted 1:1 with Tetralin. Emulsification-Demulsification experiment at 3 salinities. From left to right, 86 meq/L, 171 meq/L, and 513 meq/L. Label A is NaCl + 0.5 equiv. fraction Na_2CO_3 , label B is NaCl + 0.5 equiv. fraction NaHCO_3 , and label C is NaCl only.

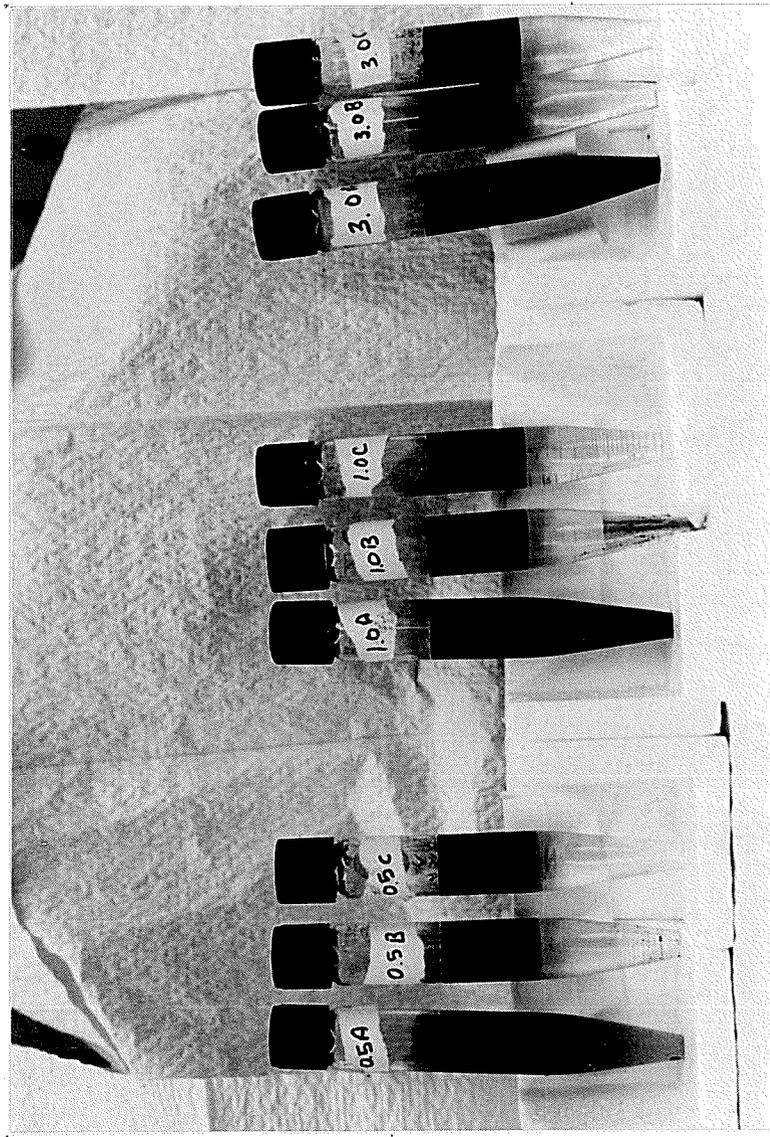


FIGURE 6. - Cerro-Negro diluted 1:2 with Toluene. Emulsification-Demulsification experiment at 3 salinities. From left to right, 86 meq/L, 171 meq/L, and 513 meq/L. Label A is NaCl + 0.5 equiv. fraction Na_2CO_3 , label B is NaCl + 0.5 equiv. fraction NaHCO_3 , and label C is NaCl only.