The Alkaline - Surfactant - Polymer Combination Flooding and Application to Oilfield for EOR

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Abstract

In order to recovery as much oil as possible from reservoir using as little chemical agent as possible, a study on the property of surfactant alkaline-polymer (SAP) combination solution has been carried out by the principle of co-ordination effect. The interfacial tension (IFT) between the solution-crude oil has close relation to chemical composition of the system and the property of crude oil. For wax-bearing oil, the combination surfactant in ASP system is formed by petroleum carboxylate and proper petroleum sulfonate. For acid crude oil, as the oil contains natural organic acid, the petroleum carboxylic soap can be formed in situ, proper petroleum sulfonate is compounded with non-ionic surfactant (triton serie). The distribution of surfatant's molecule in crude oil-surfactant solution interface and the structure of interface adsorbed film can be controlled by adjusting the pH value and the ionic strenth of the solution to form ultralow IFT. For those two systems, the transient IFT can be less than 10^{-4} mN/m and the equilibrium IFT less than 10^{-3} mN/m when the concentration of surfactant is below 0.5% (by weight). These systems show the same displacement efficiency as that of microemulsion flooding, the amount of surfactant used reduced by more than 10 times. The pilot test result of evident increase in recovery factor and evident decrease in water cut has been achieved in a development test area abandoned in an oilfield.

Introduction

In china, most oilfields are developed by water flooding, but now, the recovery efficiency is low and water cut is over 80% because of the heterogeneity of reservoirs and high viscosity of oil. SAP combination flooding is a new EOR technology developed in recent years. The aim of combination flooding is to advance the advantage of every chemical flooding methods and to overcome the disadvantage of them^[1,2,3,4]. Most studies indicate that there are complex relations between the surfactant produced by the reaction of alkaline with the natural organnic acid in crude oil and the added surfactant, alkaline and surfactant, surfactant and polymer. The organic and inorgannic addition agent control and restrict the distribution of surfactant in oil and water phase, so that the aim to control the formation of ultra-low IFT can be practiced. At the same time, alkaline will effect the loss of surfactant in reservoir. So that high efficiency displacement system can be obtained by adjusting the relations of them reasonably. This paper reported results of the formula about SAP combination flooding for crude oil with high acid value and waxy crude oil. For wax-bearing oil, the combination surfactant is used in SAP system. For acid crude oil, as the oil contains natural organic acid, the petroleum carboxylic soap can be formed in situ, and proper petroleum sulfonate is compounded with non-ionic surfactant (triton serie). The distribution of surfactant's molecule in crude oil-surfactant solution interface and the structure of interface adsorbed film can be controlled by adjusting the PH value and the ionic strenth of the solution to form ultra-low IFT. For those two sys-

tems, the transient IFT can be less than 10^{-4} mN/m and the equilibrium IFT less than 10^{-3} mN/m when the concentration of surfactant is below 0.5% (by weight). These systems show the same displacement efficiency as that of microemulsion flooding, the amount of surfactant used is reduced by more than 10 times. The first SAP combination flooding pilot test, was practiced in Gudong Oil-field development test area which approaches to be abandoned, Shan-dong province, in China. The pilot test result of evident increase in recovery factor 13.4% (OOIP), and evident decrease in water cut has been obtained.

Experiments

1. Background

Crude oil used in study is stock tank oil from pilot area. The acid crude oil was obtained from Gudong oilfield, with acid value of 3.11 KOH mg/g, viscosity in place of 41.25 mPa · s, density of 0.95 g/cm³. The waxy crude oil was obtained from Da-qing oilfield, viscosity in place of 10.6 mPa · s. Water used in experiment is simulated water with ion composition in Table 1. Main characters of surfactant used are showed in Table 2. They are all commercial products. Polymer used in experiment is PHPAM in Pfizer U. S. A. (product code is 3430S and 3530S). Alkaline are chemical agents of Na₂CO₃, NaOH, nNa₂, SiO₂ (n = 1.03). Core samples were provided by the oilfield.

Table 1 Water properties of pilot field

Component	Da-qing Oilfield g/L	Gudong Oilfield g/L
NaCL	2.294	2.451
KCL	0.013	—
CaCL	0.042	0.033
Mg ₂ Cl 6H ₂ O	0.017	0.042
Na ₂ CO ₃	0.075	0.018
NaHCO ₃	1.860	0.679
Na ₂ CO ₃	—	0.058
total salinity	4.456	3.281

Table 2 Surfactant products

Product code	Active substance content %	Average molecular Weight	Salt %	Volatile mater %	Unulfonated oil %
XCY	53.6	390	1.31	6.42	39.0
WQY	51.0	400	—	—	—
AOY	50.5	380—420	—	—	—
CY-1	50.1	450	—	—	—
OP-10	99.9	—	—	—	—
LTSP	47	430—450	4.20	11.8	37.0
FYG	50	280—300	—	—	—

2. Solution characters of SAP system for acid crude oil

2.1 IFT between the SAP combination solution-crude oil

a. Surfactat types:

Activities of diffrent petroleum sulfonate sodium have been tested under same conditions (1.0% Na₂CO₃, 1000 ppm 3530S), in the manner as follows: isovolumetricly mixing of oil with combination solution, fully shaking, being laid up for 15 days at 68°C, and then testing IFT. Result is shown in Figure 1, from where it can be seen that for three types of petroleum sulfonate sodium, AOY, WOY, and XCY, IFT vary between $2 \times 10^{-2} \sim 10^{-1}$ mN/m. Addition of these petroleum sulfonate sodium didn't evident ecrease IFT, and has no synergetic effect with petroleum carboxylic soap to contribute surface activity. In concentration rang of 0.4~0.6% by weight, IFT between oil and combination solution of CY-1, LTSP is lower than $8 \times 10^{-4} \sim 3 \times 10^{-3}$ mN/m, indicating that there is synergetic effect between CY-1, LTSP and petroleum carboxylic soap formed in place. The curves of transient IFT between oil and CY-1 composite solution (0.1% 3530S, 1.0% Na₂CO₃) are shown in Figure 2, where minimum transient IFT is as low as 8×10^{-4} mN/m.

Fig. 1 Effect of surfactant type on balanced IFT

Fig. 2 Effect of CY-1 concentration on transient IFT

b. mixed surfactant

Figure 3 shows curve of the minimum transient IFT value of different combination between

CY-1 and OP-10. Rise of CY-1 content in mixture makes IFT decrease, and minimum IFT reaches 4.0×10^{-4} mN/m at the mixture of 0.1% OP-10 and 0.3% CY-1. Coordination effect of three kinds of surfactant (CY-1, OP-10 and petroleum carboxylic soap formed in place) do enhance this contribution. Appropriate mixing between them made IFT value as low as 4.0×10^{-4} mN/m.

Fig. 3 Correlation curve of IFTmin vs con. of surfactants

c. Alkaline types

Experiments compared soapnification of strong alkaline (NaOH) with that of weak alkaline (Na_2CO_3 and $\text{nNa}_2\text{O} \cdot \text{SiO}_2$). Figure 4 shows the variation curves of IFT under the condition of 0.4% CY-1, 0.1% 3530S and 1.0% alkaline. For these kinds of alkaline, the abilities to reduce IFT are different, the order is: $\text{Na}_2\text{CO}_3 > \text{nNa}_2\text{O} \cdot \text{SiO}_2 > \text{NaOH}$. appropriate alkaline concentration is less than 1.0%. Under the conditions of this experiment.

Fig. 4 Effect of alkaline type on transient IFT

Table 3 Turbidity point of ASP composite system

System composition		Turbidity point, °C
Reagent	Concentration, %	
OP-10	0.4	70
OP-10*	0.4	59
OP-10*	0.2	88
CY-1	0.2	
OP-10*	0.4	87
CY-1	0.4	

* 1.0% Na_2CO_3 , 0.1% 3530S

d. Turbidity point of combination system

Adding OP-10 will cause variation of system's turbidity temperature. Temperatures of turbidity point for different systems are listed in Table 3.

2.2 Compatibility between components

Once alkaline concentration exceeds salting out concentration of surfactant (petroleum sulfonated sodium), surfactant will be salted out. Surfactant is compatible with polymer (HPAM) only under appropriate concentration^[5,7]. Table 4 shows system change after 3 months balance phase. test mixed surfactant of 0.2% CY-1 and 0.2% OP-10, coagulated matter will be 0% (volume) under condition of 0.1% 3530S.

Table 4 Compatibility between compositions of ASP system

Alkaline type	Upper phase volume %	Lower phase volume %
NaOH	97.5	2.5
Na_2CO_3	99	1.0
$\text{nNa}_2\text{O} \cdot \text{SiO}_2$	99.5	0.5

* 1.0% alkaline, 0.4% CY-1, 0.1% 3530S

2.3 Viscosity and Viscoelasticity (screen factor) of SAP solution

a. Viscosity

Figure 5 describes effect of Na_2CO_3 concentration and CY-1 concentration on viscosity of the ASP solution. The rise of alkaline concentration slightly reduces viscosity of HPAM solution, while CY-1 concentration in a range of 0.1%~0.4% has no effect on viscosity of SAP system.

Fig. 5 Effect of surf. and alkaline concentration on viscosity

b. Screen factor

Figure 6 shows screen factor of SAP solution and that of single polymer solution. It can be seen that after adding alkaline and surfactant, screen factor slightly reduced.

Fig. 6 Screen factor Curve of ASP solution

2. 4 Flooding agent loss after contacting with rock

a. Static loss^[3]

Typical experiment results are listed in Table 5. Losses for single surfactant systems CY-1 and OP-10 are respectively 2.38×10^{-3} mmol/g sand and 8mg/g sand, they reduced to 1.11×10^{-3} mmol/g sand and 3.7mg/g sand after adding alkaline and polymer, 1.62 and 2.22 mg/g for composite system (mixed surfactant). Experiment results of alkaline consume are listed in Table 6. Alkaline consume curve is principally up to Langmuir model, and alkaline loss of ASP solution is less than that of single alkaline solution.

Table 5 Static surfactant losses in ASP solution

solution composition	Loss
0.4%,CY-1	2.38×10^{-3} mmol/g
0.4%,OP-10	8.0mg/g
0.4%,CY-1*	1.11×10^{-3} mmol/g
0.4%,OP-10*	3.7mg/g
0.2%,CY-1*	1.62mg/g
0.2%,OP-10	2.22mg/g

* 1.5%Na₂CO₃,0.1%3530S

Table 6 Alkaline loss in ASP solution*

Ingredient	Loss
Na ₂ CO ₃	3.1mg/g
Na ₂ CO ₃	2.63mg/g
nNa ₂ O · SiO ₂	4.3mg/g

* 1.0% alkaline+0.4%CY-1+0.1%3530S

Table 7 Dynamic loss of surfactant in ASP solution

Injection mode	Reagent	Loss,mg/g
Continuous	OP-10	2.36
	CY-1	0.69
Slugs, 0.4PV	OP-10	0.24
	CY-1	0.1

b. Dynamic loss

Dynamic loss was measured in sandpack. CY-1 and OP-10 concentrations flow out liquid were analysed with HPLC. Results are listed in Table 7, where loss during flow process is less than static loss.

3. Solution characters of SAP flooding system for waxy crude oil

3.1 Study of petroleum carboxylate sodium and the combination system of petroleum carboxylate with petroleum sulfonate

For Daqing waxy crude oil, the IFT between crude oil and the solution of petroleum carboxylate sodium (FYG), three kinds petroleum sulfonate sodium, and the combination system of them was researched under the simulated geological condition. Figure 7 shows the curve of transient IFT between crude oil and the mixed solution of petroleum carboxylate sodium (FYG) and alkaline (NaOH, Na₂CO₃). The transient IFT between FYG and strong alkaline (NaOH) combination solution and oil reached the 1.4×10^{-3} mN/m when the time is three minutes, then it rised immediately and rapidly. The transient IFT between FYG and weak alkaline (Na₂CO₃) combination solution and oil reached the minimum rapidly and immediately, i. e. 1.2×10^{-2} mN/m, and then it rised slowly. It can be seen that the effect of PH value on IFT between petroleum carboxylate sodium system and crude oil is obvious, and the condition of high PH value is advantage for reaching ultra-low IFT. This phenomena is regarded as that the further soapnification of petroleum carboxylate sodium in strong alkaline enviornment lead to increasing of RCOO⁻ concentration, and it is more advantage for forming the adsorbed film on interface after contact with crude oil. So that, the distribution of surfactant on the oil-water interface can be controlled by adjusting the PH value of solution and the necessary ultra-low IFT can be obtained.

1.0%NaOH, + 1.5%Na₂CO₃

Fig. 7 Transient IFT between crude oil and 0.5%FYG-alkaline combination system

The studies on IFT between crude oil and

combination surfactant (FYG—CY—1) and alkaline mixed solution showed in Figure 8 indicate as follows as:

a. Transient IFT can reach the minimum (i. e. 10^{-4} mN/m) in a moment after the mixed solution contacts with crude oil, and the equilibrium IFT can stand by 10^{-2} mN/m.

b. The effect of weak or strong alkaline on the IFT between crude oil and SAP solution (mixed surfactant) is weak.

c. The transient IFT can reach the ultra-low value, i. e. $10^{-3} \sim 10^{-4}$ mN/m, when the surfactant (FYG—CY—1) is in the rang of 1 : 4 ~ 4 : 1.

1.0%NaOH. + 1.0%Na₂CO₃
Fig. 8 Transient IFT between oil and 0.5%FYG
0.5%CY-1 and alkaline mixed solution

3.2 Machesism of alkaline in SAP combination system and the choice of alkaline type

The IFT between single NaOH or Na₂CO₃ water solution and crude oil is higher than 1 mN/m. It indicates that the ammount of nature organic acid in Daqing crude oil is little. As the same as, the IFT between single FYG or CY—1 surfactant water solution and crude oil is higher than 1 mN/m. But the transient IFT between SAP solution and crude oil can reach $10^{-3} \sim 10^{-4}$ mN/m. And then, what is the action of alkaline for waxy crude oil? Figure 8 demonstrate as follows:

a. Following the increase of Na₂CO₃ concentration, the transient IFT decreased obviously while the PH value of solution only increased slightly (10.1~10.5), but the ionic strength increased to 0.43 from 0.14.

b. As the same, comparing the two combination systems which consist of 0.5% CY—1—1.0% Na₂CO₃ and 0.5% CY—1—1.0%NaOH, the PH value of next is much more higher than that of last, the ionic strength of them is simillarate.

c. Replacing the alkaline with the same ionic strength salinity (NaCl), inspite of the PH value of mixed solution is about 7, but the minimum IFT of the system can reach 10^{-4} mN/m also.

To sum up, the action of alkaline in SAP solution flooding system is to improve the ionic strength of system and to adjust the distribution of surfactant in water and in oil phase. IFT can reaches the minimum when distribution ratio in wter and in oil attends to 1.

Table 8 Parameters and results of oil replacement

		Effective Permeability μm^2	Initial oil Saturation %	Injection Speed ml/h	Composition of injection slug			injection mode pv	Oil recovery, % OOIP			Total oil recovery % ROIP
					S	A	P		water flooding	chemical flooding	total	
Sheng-li crude oil	1	2.99	77.8	14.0	0.4	1.0		0.2				
					0.4	1.0	0.1	0.2	67.5	15.8	83.3	48.5
							0.1	0.2				
Da-qing crude oil	2	3.019	71.7	14.0	0.4	1.0	0.10	0.3	71.3	9.5	80.8	33.3
							0.08	0.2				
Da-qing crude oil	1	0.962	63.4	12.0	0.5 *	1.48 *	0.12	0.3	48.0	17.7	65.7	35.5
							0.08	0.2				
Da-qing crude oil	2	0.961	69.0	12.0	0.5 *	1.48 *	0.12	0.3	55.8	18.4	74.2	41.7
							0.08	0.2				
Da-qing crude oil	3	0.935	69.4	12.0		1.48 *		0.2				
					0.5 *	1.48 *	0.12	0.3	62.3	17.2	79.5	45.6
							0.12	0.2				

* S—0.3%FYG—0.2% CY—1
A—1.2%Na₂CO₃—0.28%NaOH

Fig. 9 Effect of ionic strength and pH on transient IFT

Base on these studies, alkaline agent in the formula of FYG and CY-1 combination system was determined to be 0.28% NaOH and 1.2% Na₂CO₃. Not only the PH value of system, but also the ionic strength of system can be adjusted applying the mixed alkaline.

4. Flooding evaluation with physical simulation

SAP solution flooding experiments were carried out under the simulated geological conditions. The results showed in Table 8 indicate two points. One is that for Gudong oilfield, the optimum formula is consist of 0.4% surfactant, 1.0% Na₂CO₃ and 1000 ppm 3530S polymer. SAP flooding recovery is 18.4% (OOIP) and 48.55% (ROIP), obvious rich oil zone was observed after flooding slug, surfactant and polymer was tested after rich oil zone, and themanner of mlti-slug is benifit to enhancing oil recovery. The other is that for Daqing oil field, the optimum formula is consist of 0.3% FYG, 0.2% CY-1, 0.28% NaOH, 1.2% Na₂CO₃, and 1200ppm polymer, SAP flooding recovery is 18.4% (OOIP) and 41.7% (ROIP), the manner of multi-slug is optimum.

Field Pilot

1. Survey of the pilot area

1.1 Geology

Located in north-west of section 7 in Gudong oilfield, Shandong Province, pilot area is consist of 15 wells in 4 inverted five-spot patterns (Figure 10), with 30977 m² area, 119227m³ pore volume and 77952t reserves in place. Central well, well No.7 controls 4,944 m² area, 19893 m³ pore volume and 12,980t reservoir in place.

Fig. 10 Well location map of the samll well distance pilot in Gudong oil field

Target formation Ng5²⁺³ is a braided fluvial deposit with lithology of unconsolidated feldspar fine sandstone, mainly feldspar and quartz, 0.16 mm granularinty median, 1.48 sorted index. Dominant cement is shale in manner of contact and pore contact. Average air permeability is 3.818 μm²; effective permeability is 2.563μm²; variation coefficient of lengitudinal permeability is 0.33, wettability of rock is water wetted, initial oil saturation is 75.02%, and initial formation temperature is 68°C.

1.2 Current situation of field development

From December, 1987 to September, 1989, a water flooding was carried out. Before the beginning of the pilot, cumulative water injection was 5.06PV, water flooding recovery in well No.7 area was as high as 54.4%, water cut was 98.5%, residual oil saturatuin was only 34.2%.

2. Implement of SAP flooding pilot

2.1 Injection formula and slugs

In field implement, flooding agent intended to be injected was in four slugs (in Table 9). Main slug would be 0.35PV.

Table 9 Composition of injected slug

Composition*	Slug volume (PV)
1.5%A+0.1%P	0.05
1.5%A+0.1%P	0.05
1.5%A+0.4%S+0.1%P	0.35
0.05P	0.05

* A-Alkali, S-surfactant, P-polymer

2.2 Field implement

Pilot test started at August First, 1992. Up to Jun. 24, 1993, four slugs have been injected with cumulative injection as follows; chemical solution 70509 m³(0.592PV). On July, 1993, pilot area is converted to postwater flooding. By end of February, 1994, water cut in control producer well

area rised again to 98%, so that field pilot finished.

2.3 Results of the pilot

a. Oil production augmented and water cut declined when 0.02PV chemical flooding solution has been injected, respond could be seen, and it reached the highest peak value when 0.49PV flooding slution was injected. Oil production rises have been observed in all wells except well No. 12. Average oil production per well rised from 0.3~3.0 t/d to 5.3~27.1t/d. Oil production in pilot area rised to 76.6 t/d from 10.0t/d. Cumulative augmentation of oil production was 20667.7 t (among which 1739.5t belongs to central well No. 7). water cut in pilot area declined to 74.2% from 98% (from 98.5% to 85% for central well No. 7). Production curves are shown in Figure 11, where it can be seen that Daily production obviously increased from Feb. 1993 while water cut decreased.

Fig. 11 Production curve of well No. 9

b. Adjusted water injection profile and improved sweep area

Water injection profile in four wells was adjusted in varying degrees, for instance well No. 6 relative water intakes for three different intervals are respectively 4.9%, 13.8% and 5.0% before chemical slug injection, but 9.4%, 9.5% and 9.4% after slug injection. Monitoring by tracer injection demonstrate that four kinds of tracers injected in pour wells were observed at almost time in correspondent producers. Test of the chemicals produced at same time from nine producers demonstrate that front advance speed of chemical slugs were pratically uniform, so that chemicals could be seen at same time.

3. Monitoring during pilot process

3.1 Formation of rich oil zone during SAP flooding process

Continuous tracing test of C/O ratio spectrum in an observation well G_1 located between injector during SAP flooding process. Interpretation results are shown in Figure 12. A obvious low value of water saturation (55.2%) has been observed after injection of SAP solution. It decreased by about 10% than before injection (65.5%).

Fig. 12 Interpretation result of C/O ratio logging in observation well, G_1

3.2 Chemicals brought into play

Tracing test for chemicals in produced fluid was conducted, and results shown in Figure 11. The period of oil production augmentation is corresponding to the periods of chemical production. The loss of alkaline, polymer and surfactant (CY-1, OP-10) were calculated a 62.1%, 69.7% and (99.5%, 99.4%) respectively, higher than that in lab. experiment.

3.3 Residual oil was recovered

Analyses of physical properties and component fraction of produced oil demonstrate that surface viscosity increased from 328 to 593 mPa · s. initial boiling point (I. B. P.) raised from 241 to 285°C, composition of 200°C fraction decreased from 4.2% to 2.5%. This indicates that heavier oil was produced.

3.4 Residual oil saturation reduced and oil recovery rised

According to the calculation with several methods (material balance, C/O ration logging, single well tracing and numerical simulation, for the area controled by central well No. 7, residual oil saturation is 23.0% (OOIP) at end of pilot (34.2% before chemical slug injection). SAP flooding enhanced oil recovery by 13.4% (OOIP).

Conclutions

1. Synergetic effect between carboxylic soap formed by the reaction of alkaline in ASP solution with natural organic acid in acid crude oil, added petroleum sulfonated sodium and tritron system lead transient IFT between SAP combination solution and oil reached to 10^{-4} mN/m. For waxy crude oil, the mainly action of alkaline is to improve ionic strength of the system, and to adjust distribution of surfactant in the interface between the solution and crude oil, and to reach ultra-low IFT.

2. Flooding efficiency of SAP solution was as high as the level of micellar-polymer flooding, but with much less surfactant consumption.

3. Significant results have been obtained from pilot: water injection profile was adjusted, sweep volume improved, flooding efficiency increased, residual oil saturation declined. All these proved that using SAP flooding can further improve oil recovery of reservoirs where economic limit has been reached.

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