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**МАГИСТЕРСКАЯ ДИССЕРТАЦИЯ**

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<b>Моделирование состава поверхностно-активных веществ при прогнозировании нефтяной отдачи пласта на примере месторождений Томской области</b>	
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## **Введение**

В последние годы все чаще вводятся в разработку месторождения с трудно-извлекаемыми запасами углеводородного сырья, с неоднородными и расчлененными коллекторами. Применение поверхностно-активных веществ (ПАВ) на таких месторождениях, в добывающих скважинах, является одним из самых распространенных и эффективных инструментов повышения нефтяную отдачу. Около трети мировых запасов углеводородов можно извлечь лишь при помощи данной технологии.

Актуальность работы связана с тем, что серьезные последствия некачественного применения, а также большая стоимость самой операции, обуславливает необходимость моделирования наиболее эффективной рецептуры для уменьшения рисков и повышения эффективности поверхностно-активных веществ.

На сегодняшний день существуют способы моделирования щелочного-ПАВ-полимерного воздействия на коэффициент извлечения нефти, но они основаны на прямом измерении. То есть, зная свойства поверхностно-активных веществ, можно рассчитать прогнозируемый коэффициент извлечения нефти, но достаточно не велико число программных продуктов, которые считают в обратном порядке: зная необходимый коэффициент извлечения нефти, рассчитать рецептуру поверхностно-активных веществ. В своей работе я рассматриваю влияние одного из основных параметров – длинна углеводородной цепочки.

Целью работы является исследование влияния длинны углеводородной цепочки на коэффициент извлечения нефти. С последующим включением результатов в создание оптимального информационного инструмента для обратного моделирования структуры поверхностно-активных веществ в гидродинамических моделях месторождений.

В данной работе предоставлены результаты лабораторных исследований, в рамках которых было проведено сравнение эффективности воздействия щёлочно-ПАВ-полимерных составов на нефтяную отдачу для условий пласта месторождения.

В рамках лабораторных исследований должны быть решены следующие задачи:

1. Изучить литературу, основные критерии анализа поверхностно-активных веществ.
2. Охарактеризовать общие сведения о месторождении.
3. Рассмотреть методики исследований поверхностно-активных веществ.
4. Осуществить лабораторные тесты поверхностно-активных веществ.
5. Проанализировать полученные результаты, сделать вывод о взаимосвязи или отсутствии влияния длины углеводородной цепочки поверхностно-активных веществ на нефтеотдачу пласта.
6. Провести анализ опасных и вредных производственных факторов, возникающих при работе с поверхностно-активными веществами.
7. Рассчитать экономическую рентабельность исследований поверхностно-активных веществ.

Защищаемое положение: существует зависимость между длиной углеводородной цепочки поверхностно-активных веществ и коэффициентом извлечения нефти.

## **Аннотация**

В последние годы все чаще вводятся в разработку месторождения с трудно-извлекаемыми запасами углеводородного сырья, с неоднородными и расчлененными коллекторами. Применение поверхностно-активных веществ (ПАВ) на таких месторождениях, в добывающих скважинах, является одним из самых распространенных и эффективных инструментов повышения нефтяной отдачи. Около трети мировых запасов углеводородов можно извлечь лишь при помощи данной технологии.

Данный дипломный проект посвящен вопросу совершенствования подхода к применения поверхностно-активных веществ при прогнозировании нефтяной отдачи пласта на примере месторождений Томской области.

В первой части дипломного проекта производится обзор литературы о различных моделях, используемых при изучении нефтяных месторождений. А также критерии анализа поверхностно-активных веществ. В частности, приводится расчет и основной принцип Закона Дарси, описывается модель фильтрации, а также граничащие условия.

Во второй части дипломного проекта рассматриваются общие сведения о месторождении: геолого-геофизическая характеристика месторождения, литологический и стратиграфический анализ с характеристикой нефтяных толщ. Особое внимание уделено тектонической составляющей изучаемого месторождения.

Во третьей части дипломного проекта рассматриваются лабораторные методы исследования, применяемые при изучении поверхностно-активных веществ. Акцент сделан именно на те методы, которые возможно осуществить в рамках исследовательской лаборатории.

Во четвертой части дипломного проекта рассматриваются осуществленные исследования о фазовом поведении коммерческих образцов поверхностно-активных веществ, о их фильтрационных характеристиках, а также влиянии длины углеводородной цепочки на нефтяную отдачу.

В пятой части подводится итог проведенных исследований, производится сравнение полученных результатов исследований коммерческих образцов. Происходит корреляция данных.

В шестой части рассматривается социальная ответственность сотрудника лаборатории, при проведении исследований. Описаны основные виды вредных и опасных факторов влияния на человека и экологию. Описаны действия при чрезвычайной ситуации.

В седьмой части описывается экономическое обоснование применения поверхностно-активных веществ при повышении нефтяной отдачи пласта, а также применяемого исследовательского подхода.

## **Alkaline-Surfactant-Polymer (ASP) Flooding**

With growing global energy demand and depleting reserves, enhanced oil recovery (EOR) from existing brown fields becomes more and more important. Since most of oil fields have been under waterflooding, chemical EOR method should be easily implemented because minimum facilities are needed to add chemicals in injection water. Among chemical methods, alkaline-surfactant-polymer (ASP) is the most promising method because it has the synergy of alkaline, surfactant and polymer. In an ASP process, alkali, surfactant and polymer are added in the same solution slug.

### **ASP Mechanisms**

#### **Mechanisms of polymer flooding**

It is well known that when the viscosity of polymer solution is increased, the sweep efficiency is improved.

Another mechanism is related to polymer viscoelastic behavior. Due to polymer viscoelastic properties, there is normal stress between oil and polymer solution. Thus polymer exerts a larger pull force on oil droplets or oil films. Oil is “pushed and pulled” out of dead-end pores. Thus residual oil saturation is decreased. This mechanism was rarely discussed until recently.

One economic impact of polymer flooding which has been less discussed is the reduced amount of water injected and produced, compared with waterflooding [1]. Because polymer improves the sweep efficiency, less water is produced and injected. In some situations like an offshore environment and a desert area, water and the treatment of water could be costly.

#### **Mechanisms of surfactant flooding**

The key mechanism for surfactant flooding is low interfacial-tension (IFT) effect. To discuss this mechanism, we need to first discuss the concept of capillary number versus residual oil saturation. The capillary number,  $N_c$ , is defined as

$$N_c = \frac{u * \mu}{\sigma} \quad (1)$$

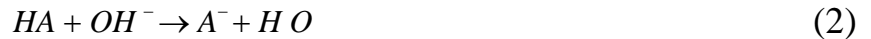
where  $\mu$  is the displacing fluid,  $u$  is the displacing velocity, and  $\sigma$  is the interfacial tension between the displacing fluid and the displaced fluid (oil). Many experimental data show that as the capillary number is increased, the residual oil saturation is decreased [2].



A typical capillary number is about  $10^{-7}$ . To reduce waterflooding residual oil saturation, the capillary number must be higher than  $10^{-7}$ . How can we increase the capillary number? From the definition of capillary number, there are three ways: (1) increasing injection fluid velocity  $u$ , (2) increasing displacing fluid viscosity  $\mu$  and (3) reducing the IFT  $\sigma$ . The injection fluid velocity is limited by pump capacity or formation injectivity. Even though the pump capacity is not a problem, if the injection velocity is too high, the injection pressure may be higher than the formation fracture pressure. Increasing injection fluid viscosity is limited at least by economics, because increasing polymer solution viscosity needs higher polymer concentration. In reality, we could not use a too high polymer concentration owing to a solubility issue. The way left is to reduce IFT. It is known that the interfacial tension between a surfactant solution and oil can be reduced from 20-30 to  $10^{-3}$  mN/m. In other words, by adding surfactants, we can practically increase the capillary number by more than 1000 times.

### **Mechanisms of alkaline flooding**

One mechanism is that a surfactant (called soap to differentiate it from an injected synthetic surfactant) is generated in situ when an alkaline solution reacts with the acid component in a crude oil. The reaction equation is



where HA is a pseudo-acid component and  $A^{-}$  is the soap component.

More importantly, when an alkali is added with a surfactant like in an ASP process, alkali can reduce the adsorption of surfactant on the grain surfaces. This makes surfactant work more efficiently and less surfactant needs to be injected. Other mechanisms include emulsification, oil entrainment, bubble entrapment and wettability reversal [3].

### **Synergy in ASP**

Some incremental oil recovery factors over waterflooding from alkaline flooding, polymer flooding and ASP flooding from laboratory. The recovery factor from surfactant flooding was not available. The recovery factors from alkaline and polymer flooding were 10% and 11.6%, respectively. The sum of these factors was 21.6%, whereas the recovery factor from the ASP was 45.3%. Even we assume the recovery factor from surfactant flooding could be 15%, the sum of the three processes would be 36.6%, still lower than 45.3%. These data clearly demonstrate the ASP synergy.

Another important mechanism is the synergy between in situ generated soap and synthetic surfactant. Generally, the optimum salinity for the soap is unrealistically low, and the optimum salinity for the surfactant is high. When they function together, the salinity range in which IFT reaches its low values is increased [4]

An incomplete list of the synergies and interactions of ASP may be summarized as follows.

1. Alkaline injection reduces surfactant adsorption.
2. Alkali reacts with crude oil to generate soap. Soap has low optimum salinity, whereas a synthetic surfactant has relatively high optimum salinity. The mixture of soap and synthetic surfactant has a wider range of salinity in which the IFT is low.
3. Emulsions improve the sweep efficiency. Soap and surfactant make emulsions stable owing to the reduced IFT. Polymer may help to stabilize emulsions owing to its high viscosity to retard coalescence.
4. There is a competition of adsorption sites between polymer and surfactant. Therefore, addition of polymer reduces surfactant adsorption, or vice versa.
5. Addition of polymer improves the sweep efficiency of alkaline and surfactants.
6. It was reported that the decrease of liquid production was not only related to the increase of the viscosity of displacing fluid, but also related to emulsification and

scaling after injection of ASP slug [5]

### **Screening Criteria**

Like any EOR method, before we consider an ASP project, we need to make sure the resources for the ASP project are available, the project is supported by the company management, and it meets local environmental regulations.

#### *Formation*

Almost all of the chemical EOR applications have been in sandstone reservoirs, except a few stimulation projects that were conducted in carbonate reservoirs. One reason for fewer applications in carbonate reservoirs is that anionic surfactants have high adsorption in carbonates and cationic surfactants are expensive. Another reason is that anhydrite often exists in carbonates which causes precipitation and high alkaline consumption. Clays in sandstones also cause high surfactant adsorption and high alkaline consumption. Therefore, clay contents must be low for a chemical EOR application.

#### *Oil composition and oil viscosity*

Oil composition is very important to alkalis and surfactants, but it is not critical to polymer. Acid number of a crude oil should be high so that alkali reacts with the acid component to generate soap. However, there is no clear relationship observed between the ASP performance and the acid number in ASP projects. There is no requirement established regarding the minimum acid number to apply ASP EOR. Chang stated that the minimum acid number should be 0.3 mg KOH/g oil [7]. In the Lagomar ASP test in Venezuela, the acid number is as low as 0.04 mg KOH/g oil. Daqing oils have low acid number as well (in the order of 0.1 mgKOH/g oil). In these cases, the main mechanism is not related to soap generation. Instead, the mechanism is related to the reduction of surfactant and polymer adsorption by injecting high-pH alkaline solution. The role of acid component in ASP should be more systematically studied. Therefore, the value of acid number is not proposed in Table 1 as a screening criterion.

#### *Formation water salinity and divalents*

Formation water salinity and divalents are critical to ASP EOR. Most of ASP projects were carried out in low-salinity reservoirs of about 10,000 ppm. Al-Bahar et al. criterion is 50,000 ppm salinity and 1000 ppm hardness. This 1000 ppm hardness is probably too high and needs extra chelating agents.

### *Reservoir temperature*

The reservoir temperature should be lower than 93 °C for A/S/P projects, but the average temperature for actual A/S field projects was 27 °C, and the average temperature for polymer projects was 60 °C although some chemical suppliers state that polymer can be applied up to 120 °C. Daqing reservoir temperature is about 45

°C. The maximum temperature for few Chinese projects was in the order of 80 °C. It seems that some ASP projects with higher reservoir temperature are being considered.

### *Formation permeability*

High permeability is favorable to ASP flooding, and it is critical to polymer injection. Simply, polymer may not be able to flow through low permeability formations. Interestingly, showed that although the criteria for chemical projects is  $> 10$  md, the average permeabilities in actual projects were 450 md for A/S, and 800 md for Polymer flooding.

As chemical products are improved, the screening criteria will be changed. From the current chemical EOR technology, extensive laboratory measurements are still needed for every project. ASP EOR in high temperature and high salinity is a challenge.

### **Laboratory Work**

There are so many kinds of laboratory tests which need to be done that in practice we could not afford to do every laboratory test needed. These are the minimum laboratory tests for almost every ASP project. The tests for polymer include the aqueous stability test, filtration test, and viscosity measurements at different shear rates. To select surfactants, the necessary test is the phase behavior test using pipettes called the salinity scan test, in addition to the aqueous stability test. One important objective from such test is to select a surfactant or surfactants that will generate a very low interfacial tension (IFT), preferably in the order of  $10^{-3}$  mN/m. Apparently, measuring IFT directly in the laboratory was preferred in China because the IFT measurements were reported in the Chinese literature for their projects. But selection of surfactants based on the solubilization ratios may be an alternative to the IFT measurement because we may use Huh's equations to calculate IFT from the solubilization ratios. For the salinity scan test, we use a fixed water-oil volume ratio which is generally one. For an ASP solution, we need to run an additional test called oil scan in which the water-oil volume ratio is changed, because alkali reacts with the acid component in the crude oil and different saturations of oil will result in different amount of surfactant

generated in situ, thus different phase behaviors. The oil scan test results are generally presented in the called activity map [4]. For a detailed description of these tests, see Sheng [1]. At the end, core flood tests are needed to see whether a significant oil recovery could be obtained. Because we only do very limited experiments, a database including measurements in earlier projects will be very useful.

Generally, all those tests mentioned above are conducted using dead oils because of difficulty to do the tests using live oils. It is the industry interest to know the effect of dissolved gas. Few papers reported the experimental work using live oils. And dissolution of methane dominated the pressure effect.

### **Numerical Simulation Work**

A proper numerical simulation work includes history-matching laboratory core flood tests to calibrate ASP flow parameters, using the calibrated or upscaled parameters in a pilot-scale, field-scale or sector model to optimize the injection schemes and to predict ASP performance, and using both the coreflood scale model and the upscaled model to do sensitivity studies and perform engineering analysis. A good example of such detailed simulation work has not been presented in the literature, partly because a good simulator which captures ASP mechanisms and is user-friendly is not available. UTCHEM, a chemical flood simulator developed by the University of Texas, is the best simulator to capture the mechanisms, but it is difficult to simulate a large field-scale case because of slow computation algorithm (sometimes solutions are not convergent) and lack of functions to include real geological features. Another weakness of UTCHEM is that it has not been equipped with visualization package for post-processing analysis.

In old days, a simulator called GCOMP developed by PHH Petroleum Consultants Ltd. was used in simulating ASP projects. These days, people start to use STARS developed by Computer Modeling Group. Actually, REVEAL developed by Petroleum Experts may also be used to simulate the ASP process.

### **Summary of Pilots and Large-Scale Applications**

It is impossible to present detailed project description and results in this paper. Detailed data are presented in our Chemical EOR knowledge Database. Here we only summarize the main results of pilots and large-scale field applications.

### **Single well tracer test before a pilot**

Before carrying out a field pilot, generally a single well (chemical) tracer test (SWTT or SWCT) is conducted. The SWTT is sometimes called chemical huff and puff. During a SWTT, a slug of ASP solution is injected in a well and the oil saturation before and after the chemical injection is measured. The main objective is to see how much oil saturation can be reduced. Generally polymer is not added in the slug. Such test is less expensive, but there is an uncertainty in estimating oil saturation, and limited information regarding interwell connectivity, sweep efficiency and injectivity can be obtained. When a field pilot is conducted, more expensive observation wells may be drilled.

### **Summary of ASP projects**

About 21 ASP field pilots and large-scale applications have been reported with performance data so far worldwide. These projects are listed in Table 2. Note that other combination processes such as alkaline-surfactant (AS), alkaline-polymer (AP) and alkaline-surfactant-polymer-foam (ASPF) are not included in this review. The former Soviet Union was active in chemical EOR, but the current status is unknown because field case studies have not appeared in the modern English literature. Thus the Russian projects are not included in this review. Among these 21 ASP projects, 12 projects were carried out in China, 6 in USA, 2 in India and 1 in Venezuela. All the projects were carried out in onshore reservoirs except the Lagomar project in Venezuela which is in offshore. It was also reported that ASP flooding was conducted recently in the Elk Hills field in California and the Taber South in Canada, but the detailed results are not available. The Marmul field has been put in polymer flooding. It was reported that an ASP pilot is being planned. Mangala was reported to have an ASP project [6]. Several papers have been presented about the design and preparation of the offshore ASP pilots in two fields, St. Joseph in Malaysia and La Salina in Venezuela. The field status was not reported in the literature.

Most of the field ASP projects were conducted in either five-spot patterns or inverted five-spot patterns. The Lagomar pilot was in an inverted seven-spot pattern; the Jilin Hong-Gang pilot was in an inverted 13-spot pattern; and the Sa-bei was in a four-spot pattern. Most of the pilots were in small scales with a few injectors used. The largest ASP project so far was the Xingbei Xing-2-Zhong project in Daqing with 17 injectors and 27 producers. The average values of important parameters are listed in Table 1.

All the ASP projects were carried out in sandstone reservoirs. For chemical EOR in carbonate reservoirs, many polymer projects were conducted in 60s – 90s. During this period, there were only a few surfactant-polymer (SP) projects, but no ASP project was reported. From 1990s – 2000s, no chemical flood projects were reported, except four surfactant stimulation projects reported

### **Injection scheme and amount of chemicals injected**

The injection schemes and amount of chemicals injected in all the ASP projects are shown in Table 3. A typical ASP injection process has three slugs: pre-slug, main ASP slug and post-slug. The function of a pre-slug is to inject polymer solution for profile improvement. Sometimes, alkaline slug is injected as a pre-slug. Its objective is to remove high- concentration divalents to avoid association of these divalent with the subsequent surfactants. Sometimes, the injected alkalis can react with divalents so that insoluble precipitates are generated. The precipitates reduce permeability; thus sweep efficiency is improved, as suggested by Sarem [10]. This process is known as mobility-controlled caustic flood (MCCF). However, as shown in Table 3, not all the projects had pre-slugs. The average injected pre-slug pore volume (PV) was 9.7% PV and the average polymer (P) concentration was 0.145 wt.%.

The main slug consists of alkali (A), surfactant (S) and polymer (P). The average injection concentrations of these chemicals were 1.25 wt.% A, 0.27 wt.% S and 0.135 wt.% P, respectively, and 30.8% PV was injected.

After the main slug is injected, if only water is injected, the water will finger into the main ASP slug, because water mobility is much high than that of ASP slug. To avoid the fingering, a post-slug of polymer is injected immediately following the main ASP slug. In some cases, a graded or tapered scheme that is an empirical model. The reason is that the chase water would have less opportunity to break through the polymer slug ahead of it if the polymer slug is large. The average injected post-slug was 24.2% PV and the average polymer concentration was 0.08 wt.%. In general, incremental oil recovery over waterflooding would increase with the amount of chemicals injected [11], also as shown later in Fig. 3. Although post-slug polymer flooding is more practiced, for the same amount of polymer to be injected, analyzing field data indicated that placing polymer in the pre-slug was better than placing in the post-slug [12].

The total chemical injected can be described by the injection pore volume multiplied by the chemical concentration. For all the projects, the injected alkali, surfactant and polymer averaged 43.16, 9.44 and 5.25, respectively, if both the PV and chemical concentrations were in the unit of percentage (%).

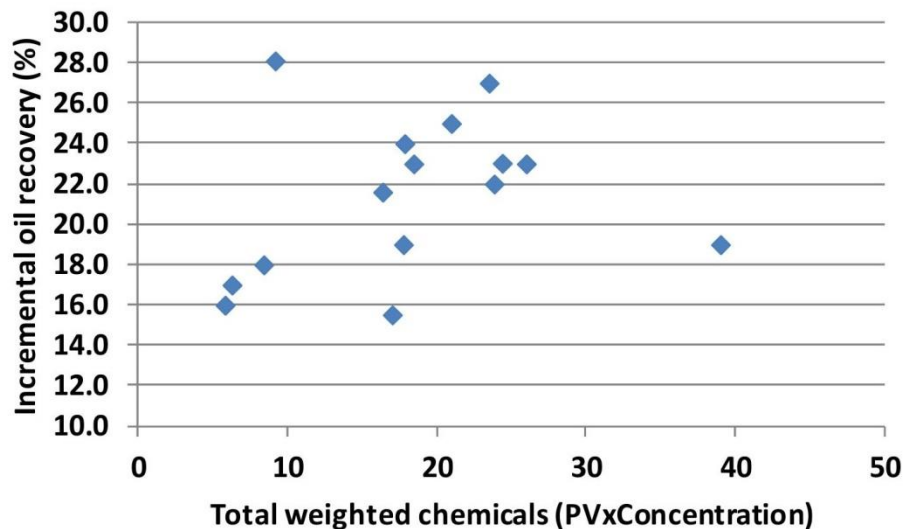


Figure – 3 – Incremental oil recovery factors versus the total amount of weighted chemicals injected

### Field performance

The incremental oil recovery factors over waterflooding available for the projects are shown in Fig. 1.

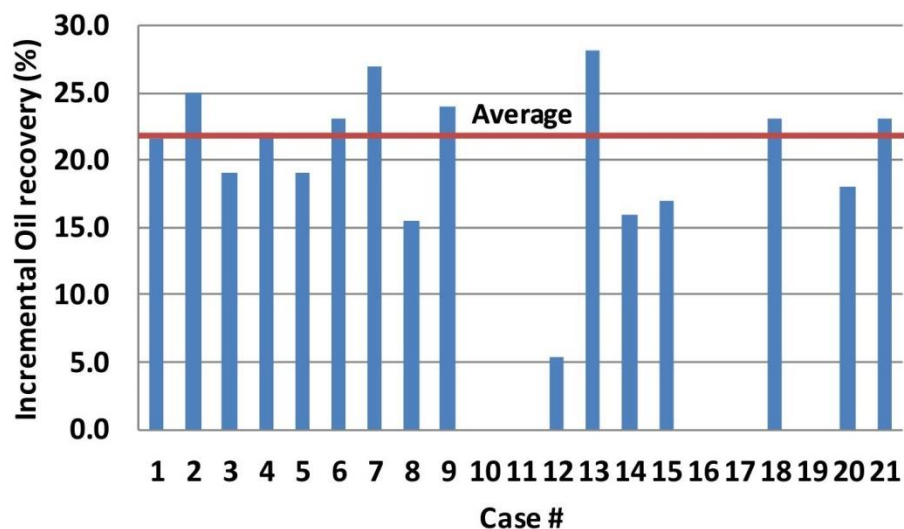


Figure – 1 – Incremental oil recovery factors available for the projects and their average



The average incremental recovery factor was 21.8% OOIP. The decreases in water cut after ASP injection available for the projects are shown in Fig. 2. The average decrease was 18% OOIP. Fig. 3 shows the incremental oil recovery factors versus the total amount of weighted chemicals injected. The total amount of weighted chemicals is calculated by the weighted sum of alkali, surfactant and polymer injected in pore volumes multiplied by their respective concentrations. The weights for A, S and P are 0.1, 1, and 0.5, respectively, which is based on their approximate prices in the market. In this figure, the highest amount of chemicals injected in the Yumen Lao-jun-miao field is not included. The figure shows that with more chemicals injected, higher incremental oil recovery factors were obtained overall.

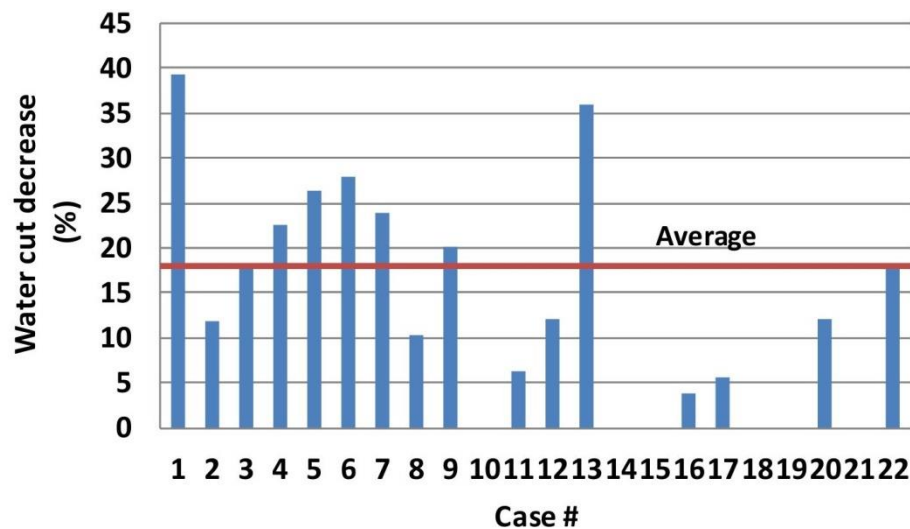


Figure – 2 – Decreases in water cut available for the projects and their average

Only limited data are available about produced chemical concentrations. The normalized produced alkali, surfactant and polymer concentrations were 0.07, 0.05, and 0.38, respectively. The normalized concentration is defined as the produced concentration divided by the injected concentration.

### **Project Economics**

Fig. 4 shows the available chemical cost per barrel of incremental oil from the surveyed ASP projects.

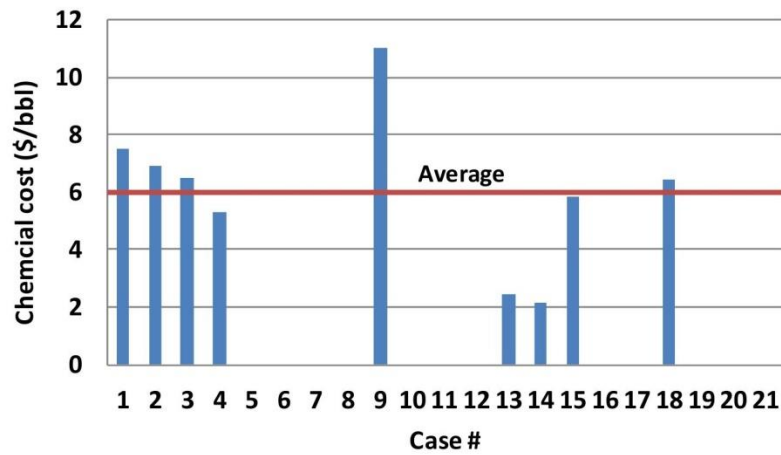


Figure – 4 – Chemical costs in actual ASP projects

The average was about \$6/bbl. We further did an estimate based on 21.8% incremental oil recovery and the average chemical slug sizes and concentrations from actual ASP projects as reported above. The chemical costs are from Chang et al [7]. The results are shown in Table 4. It shows that the average chemical cost is \$4.93/bbl which is line with the actual average cost. This is only the chemical cost and the facility cost and operation cost are not included. If the chemical costs are changed, we can simply use this table to have an estimate. When ASP is injected, less water will be produced. Here the cost saving from less water injection is not included.

### Chemicals Used

For the 21 ASP field projects surveyed,  $\text{Na}_2\text{CO}_3$  was used in 14 cases,  $\text{NaOH}$  was used in 6 cases, and  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  were combined in one case. In earlier projects,  $\text{NaOH}$  was used in Daqing projects. Silicate precipitates are generally hydrated, flocculent, and highly plugging even at low concentrations. Carbonate precipitates are relatively granular and less adhering on solid surfaces [8]. Thus sodium carbonate shows less degree of permeability damage in the presence of hard water under similar conditions. Moreover, carbonate scales can be successfully removed at production wells by acidizing or by using inhibitors, but no long-term treatment exists to control silicate-containing precipitation. This is probably one reason that sodium orthosilicate was not frequently used in chemical flooding.

As the scaling problem was experienced in some projects, the weak alkali was more and more used. To minimize the corrosion and scale problems associated with inorganic

alkalis. The organic alkali is derived from the sodium salts of certain weak polymer acids. No field test using organic alkali was reported.

Different surfactants were used in the field ASP projects. The surfactants used included ORS-41HF, ORS-46HF, ORS-62, a bio-surfactant, OP10 and CY1 (local Chinese products), BES (an anionic surfactant), lignosulfonate, KPS-1 (anionic surfactant which was a local Chinese product), dodecyl sulfobetaine (DSB), YPS-3A (local petroleum sulfonate), Petrostep B-100, TDA-13PO-SO<sub>4</sub>, and C<sub>20-24</sub> IOS. Some cosurfactants were used, for example, isobutanol (IBA), N-butanol, and isopropyl alcohol. In terms of chemical EOR in carbonates, much more surfactants were tested in laboratory and some were used in fields.

Only in one case was a biopolymer, xanthan, used. In the rest of projects, HPAM type of polymers were used. The commercial names of these polymers included 1275A, 3530S, Alcoflood 1175A, and Pusher 700.

### **Water Quality**

In Daqing ASP projects, fresh water was used initially. In some cases, produced water was re-injected at later stages of the projects. Hernandez et al. (2003) proposed that the water to be used in the ASP preparation should meet the following requirements:

- Suspended solids limit: < 0.5 ppm, 5 ppm for  $k < 100$  md; 10 ppm for  $100 < k < 300$ ; 15 ppm for  $300 < k < 600$ ; 20 ppm for  $k > 600$  md [12]
- Particle size: < 5 $\mu$ m (the size of filters used water source lines in Daqing was 20  $\mu$ m.)
- Dissolved oxygen: < 20 ppb (50 ppb required in China)
- Total hardness (Ca<sup>2+</sup> and Mg<sup>2+</sup>): <10 ppm
- Iron concentration (Fe<sup>3+</sup>): < 1 ppm (0.5 ppm in Daqing)
- Microorganisms and bacteria control

The oxygen content in solution should be low. However, dissolved oxygen in the Daqing mixing and injection system was high, and it seemed that such high oxygen did not cause serious problem. Daqing sand has 0.25% pyrite and 0.5% siderite. These minerals effectively removed the dissolved oxygen within a day and in a short moving distance from injector. Similarly, the dissolved oxygen content (3-8 ppm) in the Suriname Tambaredjo polymer project might not cause a serious problem because the sand had up to 12% siderite and pyrite.

## Salinity Gradient

In surfactant flooding, it was believed that a negative salinity gradient was needed. The negative salinity gradient means the salinities of pre-flush water slug, surfactant slug, and post-flush slug (polymer solution and/or water drive) are in descending order. The negative salinity gradient was proposed based on the relationship that the optimum salinity decreases as the surfactant concentration is decreased [4]. Because of surfactant adsorption and retention, the surfactant concentration will be decreased as the surfactant solution moves forwards. If the optimum salinity decreases with surfactant concentration, then the optimum salinity also decreases as the surfactant solution move forwards. Thus, the decreasing salinity will be consistent with the decreasing optimum salinity so that the optimum salinity is maintained as the surfactant solution move forwards. As Sheng discussed, some surfactants exhibit higher optimum salinity as the surfactant solution is diluted. In other words, the surfactant optimum salinity will be increased as the surfactant solution moves forwards [1]. Following the same reasoning, we would need a salinity gradient opposite to the negative salinity gradient (positive salinity gradient).

The reasoning for the negative salinity gradient is that a higher-salinity slug forms an oil external microemulsion which has a higher viscosity so that it would mitigate surfactant fingering ahead. One problem to form a high-salinity slug ahead of the surfactant slug is that a pre-flush water slug of a high salt concentration needs to be injected in an originally low salinity reservoir. This will result in an additional cost for the project.

Sheng did simulation study to investigate this issue. He found that the negative salinity gradient is not necessary [1]. He also proposed an optimum salinity profile which has the following characteristics:

- The optimum salinity is within the optimum phase type which corresponds to the highest oil recovery, not necessarily within the type III microemulsion.
- The optimum salinity must be used in the surfactant slug.
- Two guard slugs with the same optimum salinity are placed immediately before and after the surfactant slug. The optimum salinity in the guard slug before the surfactant-polymer slug is preferred but not mandatory.
- The salinity in the post-flush must be below the lower salinity bound of Type III.

His simulation results show that the optimum salinity profile can always lead to the highest oil recovery compared with different salinity schemes, especially higher than that from the corresponding negative salinity gradient (12.3% higher in the simulation results).

It is known that the optimum salinity of the soap in situ generated by alkaline reaction with the acid component in a crude oil is lower than that of a synthetic surfactant. Therefore, in the beginning of an ASP flood, as the crude oil saturation is higher, the optimum salinity of the mixed surfactant system will be lower so that it would be easier to have an over-optimum system. If the formation water salinity is higher than the optimum salinity in the surfactant slug, salt diffusion will lead the surfactant system much higher than the optimum salinity, which is not desirable.

### **Problems Associated with ASP Flooding**

Common operational problems in an ASP project are low injectivity, polymer degradation, difficulty to separate produced water from oil, pump failures, bacterial growth, corrosion, problems related logistics and handling, especially in an offshore environment [13]. This section discusses some issues resulting from ASP applications, including produced emulsion, chromatographic separation, precipitation and scaling.

### **Produced emulsions**

Stable emulsions can be formed in surfactant, alkaline, and even in water injection. In water injection, stable emulsions can be formed because crude oil has natural emulsifiers such as asphaltene. In surfactant injection, surfactant reduces the water/oil interfacial tension so that stable emulsions can be formed. In alkaline flooding, stable emulsions can be formed because alkali reacts with crude oil to generate in situ surfactant (soap). Although polymer helps to stabilize emulsions, it cannot form emulsions with oils. According to their structures, there are four types of emulsions: W/O, O/W, W/O/W and O/W/O. Sometimes, W/O/W and/or O/W/O are called multiple types. Generally, W/O emulsion was much more stable than O/W emulsion [1].

Emulsification is an important mechanism in alkaline flooding [3]. In other words, emulsion in ASP flooding could improve oil recovery. reported that emulsification increased the oil recovery factor by about 5% in their corefloods. Many wells in Daqing ASP applications showed that if the produced fluids were more emulsified, the decrease in

water cut would be higher. The disadvantages of emulsification are that it increases injection pressure and decreases water injection rate and liquid production rate. It also can cause difficulties in transportation and oil/water separation. In a Shengli Gudong ASP pilot test started in 1992, it was difficult to separate water from oil even though the weak alkali  $\text{Na}_2\text{CO}_3$  was injected. Overall, the advantages of emulsions appear to be greater than the disadvantages [9]

### Chromatographic separation of alkali, surfactant and polymer

Fig. 5 is the effluent concentration histories of an ASP slug injection. The vertical axis shows the normalized concentrations of polymer, alkali and surfactant. The horizontal axis is the injection pore volume. First we can see that polymer broke through first, then alkali followed by surfactant. Second, each maximum relative concentration depended on its retention or consumption in the pore medium. The maximum polymer concentration was 1, the maximum alkali concentration was 0.9, and the maximum surfactant concentration was 0.09 in this case. Third, their concentration ratios in the system were constantly changing. In other words, the chemical injection concentrations will not be proportionally decreased.

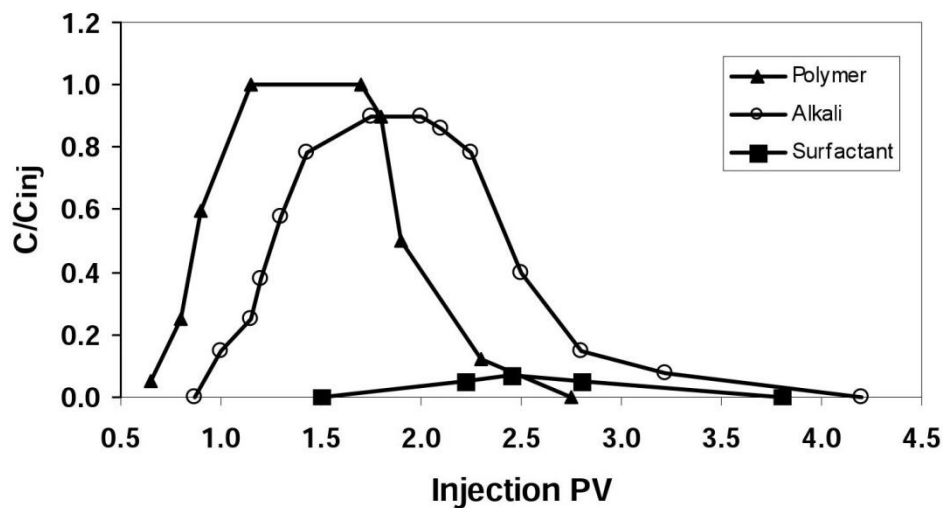


Figure – 5 – Effluent concentration histories of polymer, alkali and surfactant

Because of the inaccessible pore volume (IPV), polymer may even transport faster than the aqueous phase. Polymer will break though earlier than surfactant and alkali. In general, actual effluent concentrations and breakthrough times depend on their individual balance between the injection concentration and the retention or consumption.

To have the ASP synergy, the three components should transport at the same velocity. We cannot get rid of IPV or change retention too much to solve the separation problem. What we can do is to change the injection concentrations. Here is a simulated example. Initially, the injection scheme is 0.5 PV slug of 0.7%  $\text{Na}_2\text{CO}_3$ , 1% surfactant and 0.15% polymer. Fig. 6 shows the pH which represents alkaline concentration, and surfactant and polymer concentrations of the produced fluids.

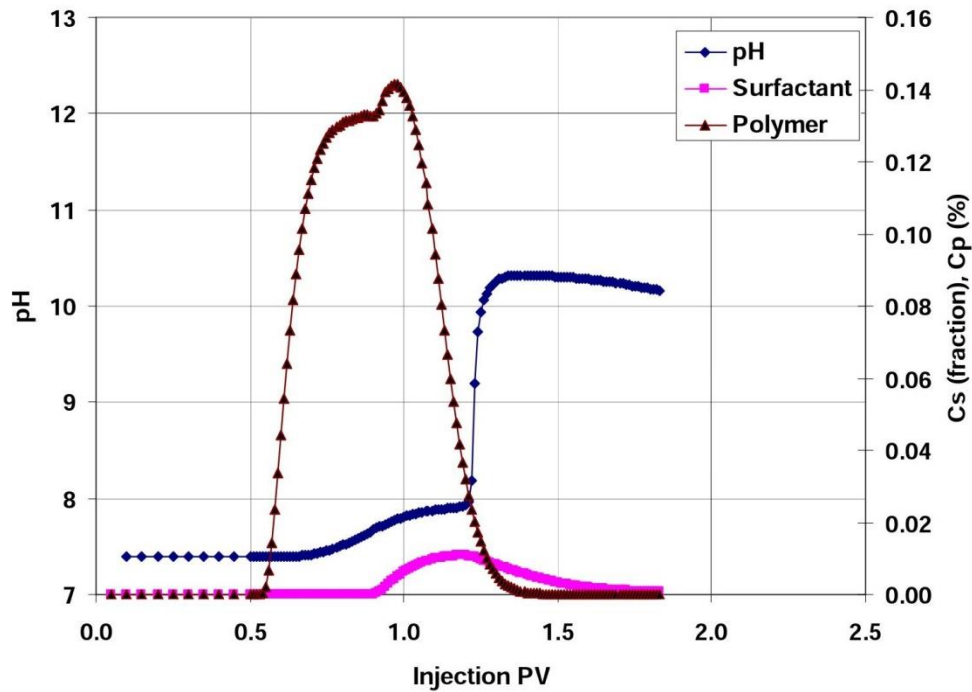


Figure – 6 – Concentration histories of the produced fluid at the initial injection concentration

Polymer breaks through first, followed by surfactant and alkali.

If we only change the alkaline concentration from 0.7% to 1.8 %, keeping the other injection concentrations and the slug volume same as the initial case, the produced concentrations are shown in Fig. 7. Now the alkali and surfactant break though the production end at the same time, although polymer still transports ahead of them. This example demonstrates that we can change injection concentrations to solve separation problem.

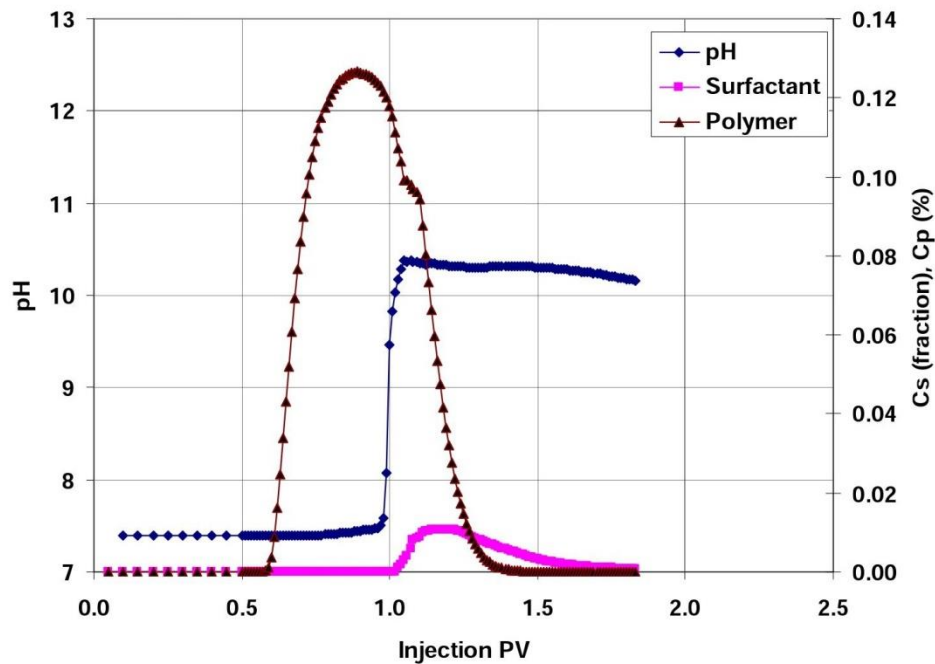


Figure – 7 – Concentration histories of the produced fluid when alkaline injection concentration is increased

### Facility problems

Because of scaling problem of ASP solution, the average work life of screw pumps in Daqing ASP flooding was shortened to 97 days, compared with 375 days in polymer flooding and 618 days in waterflooding [14].

Other facility problems associated with ASP are related to polymer viscoelastic behavior. Because of polymer solution viscoelastic behavior, when polymer solution flows into a branch line (at a tee section), a “pulling force” tries to pull the solution back into the main supply line. This pulling force increases with the increase in velocities of the branch and main supply lines. The velocity in the branch line oscillates, when the triplex pump pumps. The oscillation of the velocity changes normal stress and extension viscosity, thus causing the pump vibration. The solution was to increase pipe size [14].

The polymer solution causes a larger blind area in the bottom of a maturation tank, which makes mixing more difficult and consumes more energy to mix polymer solution. Re-design of the mixing blades mitigated the problem. For beam pumps, polymer solution enhances the sucker-rod eccentric wear. The centralizers were used to solve the problem [14]



<b>Table 1 – Summary of screening criteria for ASP</b>											
<b>Proposed by</b>	<b><math>\mu_o</math> (cP)</b>	<b><math>S_o</math> (frac.)</b>	<b>k (mD)</b>	<b><math>T_r</math> (°C)</b>	<b>Formation water salinity, (TDS, ppm)</b>	<b>Divalent (ppm)</b>	<b>Lithology</b>	<b>Clay</b>	<b>Well Spacing (ft)</b>	<b>Aquifer</b>	<b>Gas cap</b>
Lake et al. 1992	< 200										
Taber et al (1997a,b)	< 35	> 0.35	> 10	< 93.3							
Al-Bahar et al. 2004	< 150		> 50	< 70	50,000	1000	Sandstone	Low		No	No
Dickson et al. 2010	< 35	> 0.45	> 100	< 93.3	< 200,000 if $T_R$ < 60 °C, < 50,000 if $T_R$ > 60 °C						
<b>From ASP projects</b>	12.9	0.3	473.0	52	7993	178	Sandstone	Low	403.6	Weak in few cases	No
<b>Proposed in this paper</b>	< 50	> 0.3	> 50	< 95	< 50,000	< 100	Sandstone	Low	< 656	Weak	Weak

In the table,  $\mu_o$  is oil viscosity,  $S_o$  is oil saturation before ASP,  $T_r$  is reservoir temperature.

Table 2 – Summary of ASP projects worldwide						
Case #	Field	Country	Start date	P*	I*	References
1	Daqing Sa-zhong-xi (S-ZX)	China	01-Sep-1994	9	4	Wang et al., 1997; Gao et al., 1996; Li et al., 1999
2	Daqing Xing-wu-zhong (X5-Z)	China	29-Jan-1995	4	1	Wang et al., 1997; Han, 2001; Wang et al., 2006
3	Daqing Xing-2-xi (X2-X)	China	28-Sep-1996	9	4	Wang et al., 1998
4	Daqing Sa-bei-1-xi (S-B)	China	15-Dec-1997	4	3	Wang et al., 1999a
5	Daqing Xing-bei xing-2-zhong (X2-Z)	China	01-Apr-2000	27	17	Li et al., 2003; Wang et al., 2006
6	Daqing Sabei-bei-2-dong (SB-B2-D)	China	03-Oct-2004	4	3	Wan et al., 2006
7	Shengli Gudong	China	01-Aug-1992	9	4	Qu et al., 1998; Song et al., 1995; Wang et al., 1997
8	Shengli Gudao-xi	China	01-May-1997	13	6	Yang et al., 2002; Cao et al., 2002; Chang et al., 2006
9	Karamay	China	22-Jul-1996	9	4	Gu et al., 1998; Delshad et al., 1998; Qiao et al., 2000; Han, 2001; Chang et al., 2006
10	Jilin Hong-gang	China	01-Sep-1997			Zhang et al., 2001
11	Zhong-yuan Hu-zhuang-ji	China	12-Jan-2000	5	5	Jiang et al., 2003
12	Yumen Lao-jun-miao	China	01-Mar-1994	4	1	Wang et al., 1999b
13	Cambridge	USA	01-Feb-1993			Vargo et al., 2000
14	West Kiehl	USA	03-Dec-1987			Clark et al., 1993; Meyers et al., 1992
15	Tanner	USA	01-May-2000	2	1	Pitts et al., 2006
16	Mellot Ranch	USA	01-Aug-2000	3	2	<a href="http://www.surtek.com/mellotranch.html">http://www.surtek.com/mellotranch.html</a>
17	Lawrence	USA	01-Aug-2010	6	12	Sharma et al., 2012; Dean, 2011
18	Sho-Vel-Tum	USA		4	1	
19	Lagomar	Venezuela				Manrique et al., 2000; Hernandez et al., 2002
20	Viraj	India	10-Aug-2002	9	4	Pratap and Gauma, 2004
21	Jhalora	India	07-Feb-2010	6	1	Jain et al., 2012

- P and I means the number of producers and injectors.

**Table 3 – Injection schemes and amount of chemicals injected in ASP Projects**

[illegible]

<b>Table 4 – Estimation of chemical costs for a typical ASP Process</b>			
<b>Item</b>	<b>Chemical Slugs</b>		
	Pre-flush	Main slug	Post-flush
Slug Size, PV (one unit volume)	0.097	0.308	0.242
Polymer, ppm	1450	1350	800
Alkaline Agents, %		1.25	
Surfactants, %		0.27	
Alkaline cost, US\$/lb		0.12	
HPAM Cost, US\$/lb		1.03	
Surfactant cost, US\$/lb		2.2	
Incremental oil, %OOIP	21.8		
Chemical Slug Costs, US\$/bbl	0.23	4.37	0.32
Total chemical Cost, US\$/bbl Inc. Oil	4.93		

## **Заключение**

Целью настоящей работы явилось исследование влияние длины углеводородной цепочки на коэффициент извлечения нефти. С последующим включением результатов в создание оптимального информационного инструмента для обратного моделирования структуры поверхностно-активных веществ в гидродинамических моделях месторождений.

Для достижения данной цели была поставлена сетка лабораторных экспериментов для демонстрации эффективности воздействия щёлочно-ПАВ-полимерных смесей на нефтяную отдачу для условий пласта месторождения.

В рамках лабораторных исследований были получены следующие результаты:

1. Изучена литература, основные критерии анализа поверхностно-активных веществ.
2. Охарактеризованы общие сведения о месторождении.
3. Рассмотрены методики исследований поверхностно-активных веществ.
4. проведены лабораторные тесты поверхностно-активных веществ.
5. Проанализированы полученные результаты, сделан вывод о взаимосвязи или отсутствии влияния длины углеводородной цепочки поверхностно-активных веществ на нефтеотдачу пласта.
6. Проведен анализ опасных и вредных производственных факторов, возникающих при работе с поверхностно-активными веществами.
7. Рассчитана экономическая рентабельность исследований поверхностно-активных веществ.

Полученные результаты качественной и количественной оценки эффективности воздействия смеси поверхностно-активных веществ на нефтяную отдачу выявили выраженное положительное влияние на коэффициент вытеснения нефти. А также позволили качественно оценить влияние длины углеводородной цепочки на нефтяную отдачу пласта. Средняя по колонке образцов нефтяная насыщенность уменьшилась после закачки ПАВ-полимерной композиции в пределах от 10 до 20%.

Была обнаружена четкая взаимосвязь длины углеводородной цепочки и значение коэффициента извлечения нефти. С ростом длины углеводородной цепочки возрастает значение нефтяной отдачи пласта.

В ходе проведения работ, был проведен расчет экономической рентабельности исследований. Таким образом, применение данного результата в исследованиях позволяет сэкономить до 70% бюджета проекта по подбору поверхностно-активных веществ для месторождения.