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Enhanced Oil Recovery by ASP (Alkaline, Surfactant and Polymer) Flooding

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Abstract

Remaining oil in the reservoir can be divided into two classes, firstly residual oil to the water flood and secondly oil bypassed by the water flood. Residual oil mainly contains capillary trapped oil. Water flooding only is not able to produce capillary trapped oil so that there is a need for additional technique and force to produce as much as residual oil. One way of recovering this capillary trapped oil is by adding chemicals such as alkaline, surfactant and polymer to the injected water. This article presents different aspects of SAP combination flooding and discusses about one real case which SAP process successfully have been done. The crucial role of alkali in an alkaline surfactant process is to reduce adsorption of surfactant during displacement through the formation. Also alkali is beneficial for reduction of oil-water IFT by in situ generation of soap, which is an anionic surfactant. Generally alkali is injected with surfactant together. Surfactants are considered for enhanced oil recovery by reduction of oil–water interfacial tension (IFT). On the other hand, polymer is very effective addition by increasing water viscosity which controls water mobility thus improving the sweep efficiency. SAP combination flooding to enhance oil recovery is effective and economic, it can increase oil recovery rate by about 20% (OOIP) for many years. Crude oil characteristics, brine characteristics, bottom-hole temperature, alkali, well history, and treatment design are considered to maximize the treatment results.

Key Words: Alkaline, Surfactant, Polymer, Interfacial Tension, Enhance Oil Recovery.

1. Introduction

A mixture of alkali, surfactant and polymer is used in the ASP combination flooding process for tertiary recovery of petroleum. Due to the presence of natural emulsifiers, crude oil can easily form stable water-in-oil emulsion in the process of primary and secondary oil production. The stability of the crude oil emulsion is mainly determined by the oil-water interfacial film which is derived from natural emulsifiers. Crude oil emulsion, under the influence of interfacial film and crude oil viscosity, is dynamically stable. The major action of de-emulsifiers is to lower the viscosity of the interfacial film [1]. Process of emulsification, the inter-actions between the interfacial film of crude oil emulsion and the de-emulsifier added are of great importance. To realize an effective de-emulsification, it is essential for a de-emulsifier to change the properties of the interfacial film to the highest limit. Whether the film changes and how much it changes can be reflected on the interfacial tension. De-emulsifiers may also influence the stability of interfacial film. The interfacial tensions between the oil/water interfaces of ASP combination flooding fluids are relatively low.

By analyzing the continuous field tracking tests on the ASP combination flood crude oil emulsions, It was found that there are three types of crude oil emulsion by microscope equipment. They are water-in-oil emulsion (w/o type), oil-in-water emulsion (o/w type) and multiple emulsions (o/w/o type). Different emulsions are produced at different times, and fluids of different water ratios are being produced. A relatively easy emulsification between alkaline and crude oil is due to the formation of in-situ surface-active agents from the reaction of alkali and the materials in the crude oil. The de-emulsifier action mechanism is partial replacement of the interfacial active materials and lowering of the interfacial film strength.

During the development of reservoirs, especially at a high water cut stage, its economic and technical indexes will all turn worse. The water cut will increase, production rate decrease, capital construction and production costs increase. How to produce the 60~70% oil remaining underground is a task that reservoir engineers all over the world are striving to solve .In the 60~70's, petroleum professionals in many countries conducted extensive studies on polymer flooding technology.

Since oil Fields are not suitable to use thermal and miscible methods to enhance oil recovery, one of the main targets was to have breakthroughs in polymer flooding technology. After a long period of research, a more thorough knowledge of the entire polymer technology was obtained. A breakthrough was obtained on the common belief that polymer flooding cannot increase the micro-scale displacement efficiency, the visco-elastic properties of polymer fluid is the crucial factor of increasing the displacement efficiency was proposed, deepening the knowledge on polymer flooding mechanism. An optimization method to determine the molecular weight and slug size of polymer injection, well completion and multi-zone injection technology was developed. From 1995, Daqing oilfield started to industrialize polymer flooding. By the end of 1999, the annual production was more than 8 million tons of crude, Practice has shown that the polymer flooding can increase the recovery be more than 12% OOIP, its production cost is comparable to that of water flooding [1].

All the conducted SAP pilot tests, e.g. Gudong, karamay, Cambridge Minnelusa, West Kiehl, Sho-Vei-Tun oil fields, have achieved effective results. Crude oil in these oil fields generally bear characteristics of colloid, high paraffin content, high viscosity and high acid value, which is favorable to form ultra-low IFT with SAP solution system, while for non-acidic paraffin oil field, whose resin and asphaltene content is low, it is difficult for the crude oil to form ultra-low IFT with SAP solution system so as to understand the mechanism of SAP complex flooding in this kind of oil field [2]. Investigation shows that: application of petroleum sulfonate fabricated with fraction of non-acidic crude oil. SAP combination flooding to enhance oil recovery is effective and economic, it can increase oil recovery rate by about 20% (OOIP) for many years and polymer flooding has been studied and field-tested in many parts of the world. However, the incremental oil recovery is only about 2~5% OOIP. The economics of many field floods are not favorable. At the same time, in the literature, because the Capillary Number of polymer flooding can only increases a few dozen times, the common concept is that it cannot mobilize the residual oil. Therefore, it can only increase the volumetric sweep efficiency, not the displacement efficiency. The above has influenced the industrial application of polymer flooding.

In the development of this technology, polymer flooding in certain conditions, increase micro-scale displacement efficiency in cores as well as volumetric sweep efficiency was proven in the lab and field.

Daqing oil field is a heterogeneous sandstone reservoir composed of “fluvial-delta system”. The reservoir temperature and formation water salinity is low, and also crude oil viscosity is well suited. The geological characteristics can help polymer flooding. 1972 through 1992, the pilot polymer flooding performed four times, resulted in that recovery efficiency was increased by more than 10%.

2. Mechanisms of ASP

2.1. Alkaline Flooding

Alkaline flooding is an enhanced oil recovery method in which an alkaline chemical such as sodium hydroxide, sodium orthosilicate or sodium carbonate is added to injected water. The alkaline chemical reacts with certain types of oils and forms surfactants inside the reservoir. Eventually, the surfactants play a big role to increase oil recovery by reducing interfacial tension between oil and water. The alkaline agents lead to the displacement of crude oil by raising the PH of the flooding water. The reaction between alkaline and acidic components in crude oil forms in situ surfactant at the oil-brine interface. Then the crude oil is mobilized by the mixture and the mixture removes oil from the pore spaces in the reservoir. Normally, alkaline flooding has been used only in reservoirs containing specific types of high-acid crude oils. The process can be modified by the addition of surfactant and polymer to the alkali which gives an alkaline-surfactant polymer (ASP) enhanced oil recovery method, essentially a less costly form of micellar-polymer flooding. Mechanisms of ASP are illustrated in Table 1.

Chemical EOR is commercially available under limited conditions such as reservoir characteristics, depth, salinity, and pH level. The high cost of chemicals and reservoir characterization studies needs to be reduced to allow expanded use of chemical enhanced oil recovery methods before full implementation can take place. The addition of silicates is an enhancement to alkaline flooding. The silicates have two main functions:

1) It is as a buffer, maintaining a stable high PH level to produce a minimum interfacial tension. 2) It improves surfactant efficiency through the removal of hardness ions from reservoir brines, thus reducing adsorption of surfactants on rock surfaces.

On the other hand, alkaline flooding is not recommended for carbonate reservoirs because of the profusion of calcium and the mixture between the alkaline chemical and the calcium ions can produce hydroxide precipitation that may damage the formation [3].

The main profits of alkaline are lowering interfacial tension and reducing adsorption of anionic surfactants that decrease costs and make ASP a very smart enhanced oil recovery process provided the consumption is not too large. By numerical simulation process, the alkaline model can be planned and optimized to ensure the proper propagation of alkali, effective soap and surfactant concentrations to promote low interfacial tension and an encouraging salinity gradient.

Alkaline flooding is a complex process where interfacial tension reduction is not always the key mechanism. Depending on the rock and crude properties, emulsification and wettability alteration can play a major role in oil recovery from mixed-wet naturally fractured carbonates [4].

Application of alkaline flooding has four mechanisms:

- "Emulsification and Entrainment" in which flowing alkali entrains the crude oil.
- "Wettability Reversal" (Oil-Wet to Water-Wet) in which change of wettability affects change in permeability that makes increase in oil production.
- "Wettability Reversal" (Water-Wet to Oil-Wet) in which we get low residual oil saturation through low interfacial tension.
- "Emulsification and Entrapment" in which movement of emulsified oil improves sweep efficiency.

Right alkali is chosen based on some factors such as price and availability at the flooding area, the PH level, the temperature and mineralogy of the reservoir and composition of the mixed water [5].

2.2. Surfactant Flooding

Surfactant flooding is an encouraging enhanced oil recovery method. After a long term water-flooding process, some amount of oil is left trapped in the reservoir due to a high capillary pressure. To get moveable oil, surfactant agents are introduced into the reservoir to increase oil recovery by lowering the interfacial tension between oil and water. Trapped oil droplets are mobilized due to a reduction in interfacial tension between oil. The coalescence of these drops leads to a local increase in oil saturation. An oil bank will start to flow, mobilizing any residual oil in front. Eventually, the ultimate residual oil is determined by interfacial tension between oil and surfactant solution behind the oil collection. Low interfacial tension (IFT) between crude oil and water is significant for successful enhanced oil recovery by surfactant flooding. Generally, main requirement of alkaline/surfactant processes is targeting of ultralow interfacial tensions. For this purpose, the right surfactant should be selected and evaluated at low and economic concentrations. On the other hand, maintaining low IFT during the displacement process is a critical challenge because of dilution and adsorption effects in the reservoir. Consequently, oil displacement efficiency will be handled by IFT change from the static equilibrium value.

Table 1.Mechanisme of ASP

Chemical	Function	EOR Mechanism
Alkali	Increase PH, which saponifies oil	Decrease IFT
Alkali	Increases ionic strength, which alters saponification PH profile	Decrease IFT
Alkali	Increase ionic strength, which alters partition coefficient	Regulates phase behavior
Alkali	Increase negative charge density on rock	Decrease adsorption of anionic chemicals
Alkali	Increase negative charge density on rock	Make rock more water-wet
surfactant	Adsorb at oil-water interface	Decrease IFT
surfactant	Forms mixed micelles with in-situ generated soap	Broadens alkali concentration range for minimum IFT
polymer	Increase water viscosity	Decrease water mobility
polymer	Adsorb onto rock decrease effective water permeability	Decrease water mobility

2.3. Polymer Flooding

Polymer flooding is an enhanced oil recovery method that uses polymer solutions to increase oil recovery by increasing the viscosity of the displacing water to decrease the water/oil mobility ratio. During polymer flooding, a water-soluble polymer is added to the injected water in order to increase water viscosity. Depending on the type of polymer used, the effective permeability to water can be reduced in the swept zones to different degrees. It is believed that polymer flooding cannot reduce the S_{or}, but it is still an efficient way to reach the S_{or} more quickly or/and more economically. Adding a water-soluble polymer to the water-flood allows the water to move through more of the reservoir rock, resulting in a larger percentage of oil recovery. Polymer gel is also used to shut off high-permeability zones. In the process, the volumetric sweep is improved, and the oil is more effectively produced Fig. 1. Often, infectivity is one of the critical factors. The polymer solution should therefore be a non-Newtonian and shear thinning fluid, i.e., the viscosity of the fluid decreases with increasing shear rate. There are three potential ways in which polymer flooding makes the oil recovery process more efficient: 1) through the effects of polymers on fractional flow.2) by decreasing the water/oil mobility ratio. 3) by diverting injected water from zones that have been swept.

The most important preconditions for polymer flooding are reservoir temperature and the chemical properties of reservoir water. At high temperature or with high salinity in reservoir water, the polymer cannot be kept stabile, and polymer concentration will lose most of its viscosity. [6]

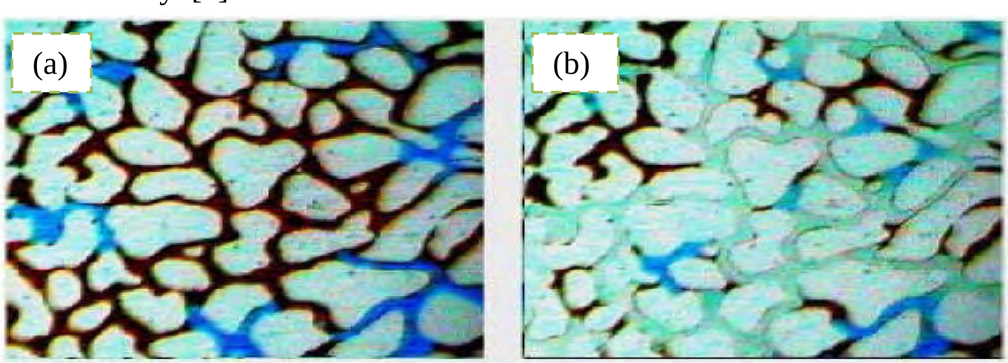

Figure 1: Comparison of oil saturation after water flooding (a) and polymer flooding (b) [7]

3. Selection of alkaline type

Result of Fig.2 shows that NaOH, Na2CO3 or NaOH/Na2CO3 have no evident influence on IFT of the system, except that alkaline concentration is relatively high when ultra-low IFT presents in Na2CO3 system. However, alkaline concentration has evident influence on system's IFT as if alkaline ,as a kind of electrolyte, determines the distribution of surfactant molecular in oil-water phase, for paraffin based oil, NaCl seems can be used to replace alkaline. This could be a kind of mechanism that paraffin based crude oil forming ultra-low IFT with oil displacing system.

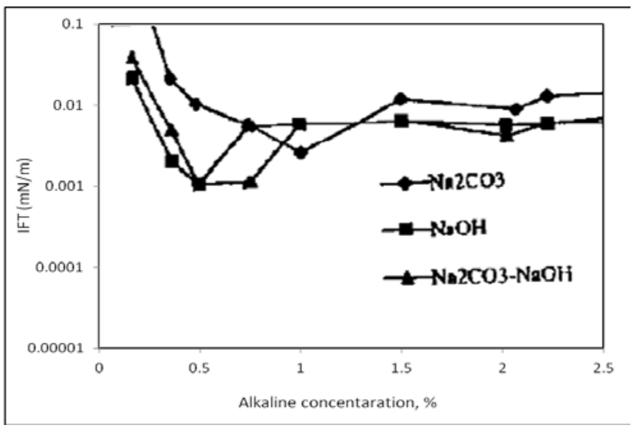

Figure2. Interfacial tension for sulfonate ASP system and crude oil with alkaline concentration at different alkaline type [6]

4. Action Alkaline system with rock

Action of alkaline with rock will not only consuming alkaline, but also damaging pore structure of rocks by dissolving them Table 2 demonstrates dissolving data of different kinds of alkaline solutions to rocks. It shows that solubility of different kinds of alkaline to Daqing cores is NaOH>NaOH+ Na2CO3>Na2CO3, with quartz and kaolinite as the main acting targets, after comprehensively considering solution action and solution interfacial activity of alkaline, it is determined that complex Na2CO3/NaOH =4:1 (note as MA) be used as alkaline agent in SAP complex solution system in the test.

Table 2. Dissolution of different kinds of alkaline to rock [6]

Minerals	Water composition	SiO_2 content, mg/l 10 days	30 days	PH 10 days	30 days
Kaolinite	Injected water	31.48	2 9	8.5	.99
	1.5% Na_2CO_3	21.86	60.7	9.9	10.6
	1.2%NaOH	433.0	472.0	12.71	12.64
	1.2% Na_2CO_3+ 0.3%NaOH	46.30	54	12.0	12.0
Quartz sand	Injected water	50.36	9.0	8.3	8.9
	1.5% Na_2CO_3	97.98	104	10.2	10.3
	1.2%NaOH	405.0	782	12.9	12.9
	1.2%Na_2CO_3+ .3%NaOH	75.52	277	2.0	12.1
Daqing core	Injected water	13.48	1 1.6	8.7	8.5
	1.5% Na_2CO_3	17.02	16.7	10.2	10.2
	1.2%NaOH	249.10	389.0	12.9	12.9
	1.2% Na_2CO_3+ 3%NaOH	197.5	74.7	12.1	12.0

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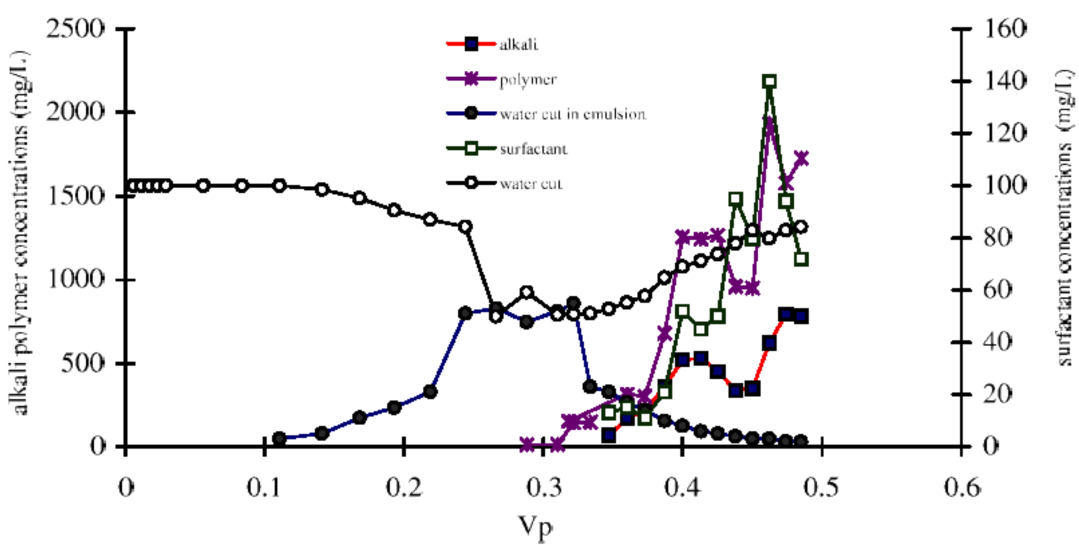
5. Emulsifying properties of the ASP combination flooding system

The curve of water cut of ASP combination flooding resultant liquid in the oil field and chemicals produced versus injected pore volumes (Vp) is shown in Fig.3 It can be seen that prior to the injection of 0.3 Vp of the ASP system, the produced liquid is mostly composed of water-in-oil emulsion. As the ASP slug system pushes forward, the chemical concentrations of the ASP components in produced liquid vary greatly with time, and crude oil emulsions, whose stability is strengthened, changes from w/o-type to o/w-type and multiple type. In the period of follow-up water drive, due to the lag behind of the surface active agent compared with polymer and alkali, oil-in-water emulsions constitutes the major part of the produced fluid and has a better stability.

In Daqing Oil Field, fluids resulting from wells vary depending on each ASP combination flood test, but its basic laws remain identical. This means that the produced fluid is water-in-oil emulsion when the water cut is lower than 50%, and oil-in-water emulsion and multiple emulsions occur because of the increase of the water cut and chemical compositions. Alkali, surfactant and water cut are principle factors to affect the formation and de-emulsification of different types of emulsions.

Alkaline water and crude oil can form a stable water-in-oil emulsion, with a type-turning point at 50% water cut. The stability of the emulsion is good. Reactions between alkali and some components in crude oil result in formation of surface active substance and thus reduce the interfacial tensions. As the alkaline concentration increases, the interfacial tensions drop sharply, however, when the concentration of alkali reaches 0.5%, the interfacial tensions basically remain constant. This shows that the amount of alkali used is sufficient to react with the crude oil. Surfactants with large oleophilic groups having a



strong oil-affinity result from reactions between alkaline water and crude oil, are rich in concentration on the alkaline water-crude oil interface, and serve as water-in-oil emulsifiers, thus making the formation of w/o emulsion easy.

Figure 3. The emulsions and chemicals change during ASP flooding [6]

Polymer can mobilize oil droplets trapped by capillary forces. The polymer fluid can pull oil out of both sides of the droplet and make the droplet get smaller. Polymer can let the oil film get thinner. Due to the fact that the velocity gradient near the pore surface is large and the viscosity of the polymer fluid is high, it can strip oil off the oil film and make it thinner. The fact that after polymer flooding of cores, the wettability changes from oil wet to water wet indirectly proves the above phenomenon. Polymer can push oil out of 'clusters'. The mobility of the polymer fluid will decrease more than a hundred times (viscosity increases 30~50 times, permeability decreases 2~3 times). This is beneficial to pushing oil out of the clusters. Measures to Increase the Elasticity of Polymer Fluids Make up the polymer fluid by low salinity water. From the relationship of the visco-elastic properties of the polymer fluid to the salinity of the make up water, it can be seen that salinity has a great effect on the elasticity of the polymer fluid.

6. Use high molecular weight polymers.

From the relationship between the visco-elastic properties of the polymer fluid and molecular weight, it can be seen that fluids made by higher molecular weight polymers have higher elasticity. Therefore, high molecular weight polymers should be used. Flooding of cores in the lab and field-tests all show that high molecular weight fluids have higher recoveries (Table 3, Fig.4).

However, too high a molecular weight polymer could block the pores in the pay zone. From tests on the compatibility of the molecular weight of polymers to the permeability of cores, it can be seen that: 1) When the mean pore radius of the core is five times larger than the mean cyclo-radius of the polymer molecule, the polymer will not plug up the core; 2) For zones of permeability higher than $300*10^{-3}$ md, using 17 million Dalton molecular weight polymers will not plug up the pay zone. Therefore, Daqing Oil Field gradually increased the molecular weight of polymer flooding from 12 million to the present 17 million Daltons.

Table 3. The effect of molecular weight on displacement efficiency[8]

Molecular Weight ($\times10^4$)	Water Flood Rec.(%)	PAM Flood Rec.(%)	Increamental Rec.(%)
2800	20.95	54.32	33.37

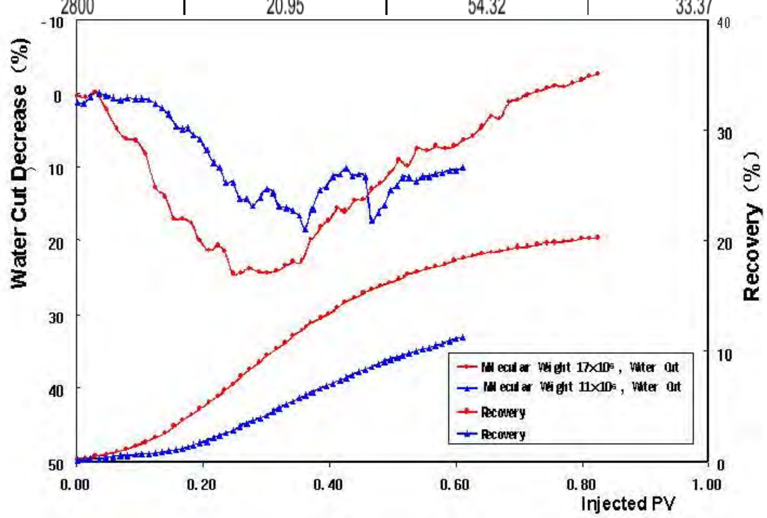


Figure 4.Effects of molecular weight on the performance of polymer flooding [8]

7. Determination of injection rate and well spacing.

In order to obtain a rather high present value of the incremental oil, the injection rate and production rate should be relatively high. But these two rates are limited by the injection pressure (it should not be above the fracturing pressure) and the minimum value of flowing pressure. Therefore, sometimes it is necessary to have a smaller well spacing to increase the production rate. The relationship between injection pressure, well spacing, injection rate and injectivity is as follows:

$$P_{max} = (L^2 \o V/180N) \qquad (1)$$

In which P_{max} is the maximum allowable injection pressure; ø pay zone porosity; V polymer fluid annual injection rate and N injectivity of the injectors.

8. Processing produced fluid containing polymer

The produced fluid contains polymer, sometimes of a concentration of 300~400 ppm. Therefore: 1) The settling time is long; 2) The polymer molecules concentrate at the oil-water interface of the emulsion and cause the interfacial film to be quite strong; 3) The polymer will increase the conductivity of the produced fluid and increase the difficulty of de-hydrating by electrical dehydrators. To solve the above problems: 1) A new type of de-emulsifier was developed, it can shorten by half the settling time and decrease the oil content in the separated water by more than 50%; 2) The structure of the electric dehydrator was changed, which increased its efficiency and resulted in stable operation.

9. Influential factors of oil displacement efficiency in pilot test

The annual production by polymer flooding after 1998 is more than 8 million tons, incremental recovery higher than 12% OOIP, at the same time, its production costs comparable to water flooding. It has obtained very good economic results.

1. Change of injectivity

After injection, flowing resistance was increases because of increasing the viscosity of injected water viscosity and retention of polymer in reservoir, and injection pressure was increased by the same injection rate. The injection pressure buildup mainly was occurred in early stage, and tended to stabilize when a given pore volume was injected, the injection

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pressure decreased when polymer absorption in reservoir reached equilibrium point. The injection pressure decreased after converting injection.

2. The change feature of polymer production concentration and water cut The early or lately produced polymer and its high or low concentration reflected the high or low flowing rate and holdup, and good or bad oil displacement efficiency in the other side.

Produced polymer concentration and changed water cut: The corresponding relation between then changes of produced polymer concentration and that of water cut in oil well was clear Fig. 5 The early polymer concentration was slowly increased but the water cut was gradually decreased after producing polymer from oil well. Polymer breakthrough and achieving well result in oil well: The polymer breakthrough time is that when the polymer solution flows through formation and arrives at oil well, the produced polymer solution concentration from oil well constantly quickly increases. Small amounts of produced low concentration polymer before this stage don’t mean the main body of polymer slug has arrived at oil well.

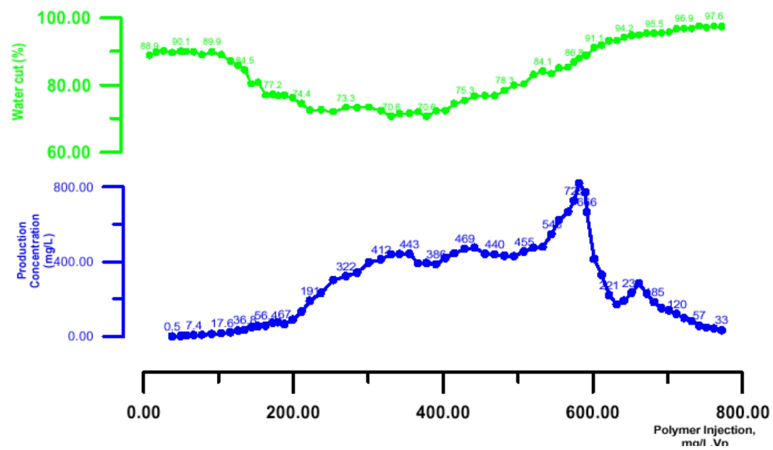

Figure 5. The curve of production and water cut [8]

There are three types when polymer is breakthrough and producer has good results: The water cut in oil well has largely lowered before polymer breakthrough .the water cut in oil well changes obviously, the polymer production is low ,the water cut in oil well don’ t decrease under lots of produced polymer. The polymer breakthrough won’ t start until achieving good results, which means that polymer can largely adjust the vertical and area heterogeneous difference in reservoir, the width of oil-bearing abundance zone developed, water cut largely decreased, and incremental oil raised.

Polymer adsorption and retention: The residual resistance factor created because the polymer solution was retained in the formation under flowing through porous medium retained polymer molecule created big resistance to water and small resistance to oil.

3. Reservoir sedimentary and interconnected conditions are important influential factors of polymer displacement efficiency. However, thinned reservoir thickness in specific well points and poor communication influenced polymer displacement efficiency.

4. Watered-out reservoir condition and remaining oil volume are main influential factors of polymer water flood. There are high remainder oil saturation, and both good area regulation and polymer displacement efficiency. Lots of remainder oil is existed in the oil

well and surrounding well points, low or less watered out thickness are large; they belong to first type of communication together with producers, and exist many effective direction.

5. High molecular weight polymer injection can increase the effect of polymer flooding [9]. In this test, the molecular weight of polymer is about 11-12 millions, some is 17-19 millions the later is high molecular weight polymer. Under the same concentration condition, high molecular weight polymers are higher viscosities, and under the same volume condition, its effect is good also. However its injectivity is poor, flowing resistance is bigger.

10. Conclusions

1. Chemical reagents and water cut are important parameters that affect the stability and types of crude oil emulsions of ASP combination flooding. When the water cut is below 50%, w/o emulsion is formed. With the increase in water cut and chemical reagent content, the w/o emulsion turns into o/w type or multiple type.

2. Alkali and surfactant strengthen the emulsifying property of ASP combination flooding.

3. The main de-emulsification mechanism is partial replacement of de-emulsifier molecules with emulsifying molecules and lowers the film intensity.

4. Before or after the polymer flooding, the core analysis data show that the polymer flooding can increase the swept volume and the oil displacement efficiency.

5. The main influential factors of polymer flooding are more or less volume of remaining oil, big or small molecular weight.

6. The technical and economical results of polymer flooding in Daqing Oil Field are both very good. Incremental recovery more than 12% OOIP, operational costs comparable to that of water flooding;

7. When SAP complex flood is used in non-acid paraffin oil field, surfactant plays an important role in activity of SAP solution system; application of petroleum sulfonate fabricated with fraction of non-acidic crude oil is effective both in technology and economy;

8. Application of mixing alkaline of NaOH and Na2CO3 can both ensure the interfacial activity of the system, and can alleviate the corrosion to formation rock. For non-acidic paraffin crude oil, it seems that alkaline play as electrolyte controlling distribution of petroleum sulfonate molecular in oil-water phase.

11. Nomenclature

SAP=Surfactant-Alkaline-Polymer
A=Alkaline
S=Surfactant
P=Polymer
mN/m=millinewton per meter, dyne/m
t/d=ton per day
mg/l=ppm
PV=Pore Volume
OOIP=Original Oil in Place
wt%=Weight Percentage
IFT=Interface tension

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