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Alkaline/Surfactant/Polymer (ASP) Flooding

This is a review article on the subject of combining tertiary oil recovery methods like alkaline, surfactant and polymer flooding in order to achieve the synergetic effect out of the different impacts which are caused by these chemicals, affect oil and water filtration in the reservoir and increase oil recovery. In the article the main theoretical concepts of EOR (enhanced oil recovery) are summarized, mechanism of alkaline, surfactant and polymer flooding technologies are explained referring to the research works which had strong contribution to the development of the tertiary oil recovery methods. Formulation of alkaline/surfactant/polymer (ASP) chemical formula for EOR is discussed as well. Importance of numerical simulation and core flood laboratory experiments for the successful implementation of ASP technologies explained in the paper. Finally several examples of ASP flooding applications throughout the world projects are presented.
Key words: alkaline, surfactant, polymer, flooding, enhanced oil recovery.

Introduction

Crude oil is still a major energy source for the current economics of the world [1]. To meet the requirements of crude oil supply, more and more efforts have been placed on not onlyexploringnew oil reservoirs, but also further improving of oil recovery from the mature reservoirs [2, 3]. The improvement of oil production from mature oil fields is an important strategy from both economic and technical points of view [1, 2, 4]. According to the oil recovery history [5, 6], there are three stages of oil extraction, which are primary, secondary, and tertiary technologies [7]. In primary stage, oil production depends on initial reservoir pressure and may result in recovery of less than 20% of original oil in place (OOIP). To prevent depletion of the reservoir pressure and to recover more oil water injection is applied. This is a secondary oil recovery stage or water flooding. Due to the rock heterogeneity and high oil viscosity approximately two thirds of the OOIPremainsunswept by injected wa-

ter. Tertiary oil recovery techniques, such as thermal, gas, chemical, and microbial approaches, have been developed and show promising results on lab scale and field scale tests [7]. Tertiary recovery technique is an important enhanced oil recovery technique based on injecting a substance that is not present in the reservoir. Chemical based enhanced oil recovery approaches cover surfactant, polymer, alkali, and combination of these chemicals called ASP and have been explored extensively because of low cost, technical simplicity, and scalability in oil field tests. The design principle of chemical methods is to consider certain properties of crude oils in the reservoir and provide one or several effects: interfacial tension (IFT) reduction, wet ability alteration, emulsification, and mobility control.

In both surfactant and alkali systems, injection of surfactants and alkaline solutions aims to convert naturally occurring naphthenic acids in crude oils to soaps what results in the improvement of oil production through obtaining ultralow interfacial tensions and forming micro emulsions. In the polymer

flooding system, addition of polymer[8]is applied to reduce mobility ratio. However, ASP flooding approach is considered to be the most promising approach since it can provide advantages over controlling the above parameters for obtaining high oil recovery rate. However, the mechanism of ASP is still not completely understood that causes difficulty in designing the ASP formula. In this review, we try to discuss the ASP system from theory to its practical application aspects [9]. Both the mechanism of ASP flooding and the performance of tertiary ASP projects are discussed. It will be a useful tutorial fora new learner and contains updated materials for experts in EOR.

Theoretical discussion for EOR

The mobility ratio [7] (M_R) (equation 1) is defined as the ratio of the mobility of displacing phase ($\lambda_{displacing\ phase}$) to the mobility of displaced phase ($\lambda_{displaced\ phase}$). The mobility of a fluid λ, is a quantitative measure of its ability to flow through channels and is equal to the permeability(k) divided by the fluid viscosity(η):

$$M_R = \lambda_{displacing\ phase}/\lambda_{displaced\ phase}=(k_w\eta_o/k_o\eta_w) \quad (1)$$

where k_w – permeability of water, η_o – viscosity of oil, k_o – permeability of oil, η_w – viscosity of water.

Theoretically, while the mobility ratio is higher than one, the displacing process is unfavorable for displacing oil. While the ratio is less than one, the process is favorable for oil to be displaced.

In the calculation of oil recovery, the overall efficiency of oil recovery [7] (E_{tot}) is the main parameter for comparison of oil production efficiency. It is defined as the ratio of the recovered amount of oil (N_{ex}) to the original amount of oil in place (N_{ooip}) (equation 2) and includes the two separate efficiencies, which are the volumetric sweep efficiency (E_{vol}) and the displacement efficiency (E_{dis}), as shown in the equation 3.

$$E_{tot} = N_{ex}/N_{ooip} \quad (2)$$

$$E_{tot}=E_{vol}E_{dis} \quad (3)$$

The volumetric sweep efficiency E_{vol} is the fraction of the volume swept by the displacing agent to the total volume of the flooded reservoir. This value characterizesa macroscopic displacement effect and is a function of the mobility ratio.

Therefore, mobility control methods, including polymers, foams and alternate water and gas injection (WAG process) are applied to improve sweep efficiency. Therefore, the addition of a polymer can be applied to reduce the mobility ratio through increasing the viscosity of water and reducing permeability to water in ASP floods, which allows greater volumetric sweep efficiency. The commonly used polymers are water-soluble polymers, which include partially hydrolyzed polyacrylamide (HPAM) and xanthan gum (a biopolymer).

The displacement efficiency, E_{dis}, is the ratio of the recovered amount of oil to the amount of oil initially present in the swept volume and is a result of the microscopic effects. It is expressed as follows:

$$E_{dis}= (S_{oi}- S_{or})/ S_{oi} \quad (4)$$

where S_{oi} – initial oil saturation and S_{or} – residual oil saturation after oil recovery process.

The residual saturation of a displacement phase is related with viscous forces, surface forces (interfacial tension) and capillary number [10]. The capillary number [7], N_{cn}, is defined as a dimensionless ratio of viscous to local capillary forces(equation 5). During water flooding, some oil still remains in the reservoir, which is the residual saturation [11]. The viscous force helps to mobilize the oil, while the capillary forces cause trapping of the oil droplets due to the high IFT between water and oil.

$$N_{cn}=Viscous\ forces/Surface\ forces = \nu\eta/\delta \quad (5)$$

where ν – velocity; η – viscosity; and δ – interfacial tension.

A typical water flood capillary number is 10^{-7}. A capillary number between 10^{-4} and 10^{-3} is required to enhance oil recovery. Therefore, in order to reach the above capillary number for enhancing oil recovery, it is necessary to reduce interfacial tension from 1,000 to 10,000 folds [10].

Figure 1 shows that increasing capillary number reduces the residual oil saturation. Low residual oil saturations indicate high efficiency of oil extraction, thus large capillary number is beneficial for high displacement efficiency. Capillary number is usually in the range of $10^{-3}$when the residual oil saturation is close tozero. The most efficient way to increase the capillary number is to reduce the IFT.

Therefore, the principal objective of the ASP process is to lower the interfacial tension so that the displacement efficiency will be improved.

Presence of residual oil saturation in fractured, oil-wet formations is mainly due to the capillary forces and phenomenon of wet ability. Therefore, the height of the capillary retained oil column is greater for the narrower pores as shown by the equation (6).

$$\Delta \rho g h = -2 \delta \cos\theta / R \qquad (6)$$

By altering the wet ability to the water-wet condition and reducing the interfacial tension to ultra-low values [4], it is possible to enhance oil recovery and provide a solution to oil retention problem. An injected fluid is required to be injected into the matrix of a fractured formation for EOR rather than into the fractures. The injected fluid must be spontaneously imbibes from fracture system into the matrix. Although spontaneous capillary

imbibitions is an important mechanism for enhanced oil recovery, buoyancy will tend to allow oil to flow upward and out of the matrix into the fracture system in the ultra-low interfacial tension system. Imbibitionis a fluid flow process of increasing wetting phase saturation in a porous media. Spontaneous imbibition drives the wetting phase into the rock with no external pressure. Furthermore, in a water-wet reservoir, water will spontaneously imbibe into smaller pores to displace oil, but in an oil-wet reservoir, capillary forces inhibit spontaneous imbibition of water. The injected fluid will replace the displaced oil in the matrix and thus the spontaneous imbibition will continue as long as oil flows out of the matrix. The primary driving force for imbibition in strongly water-wet conditions is the capillary pressure. Reduction of interfacial tension reduces the contribution of capillary imbibition. Application of a surfactant alters wet ability and enhances spontaneous imbibitions (Fig. 1).
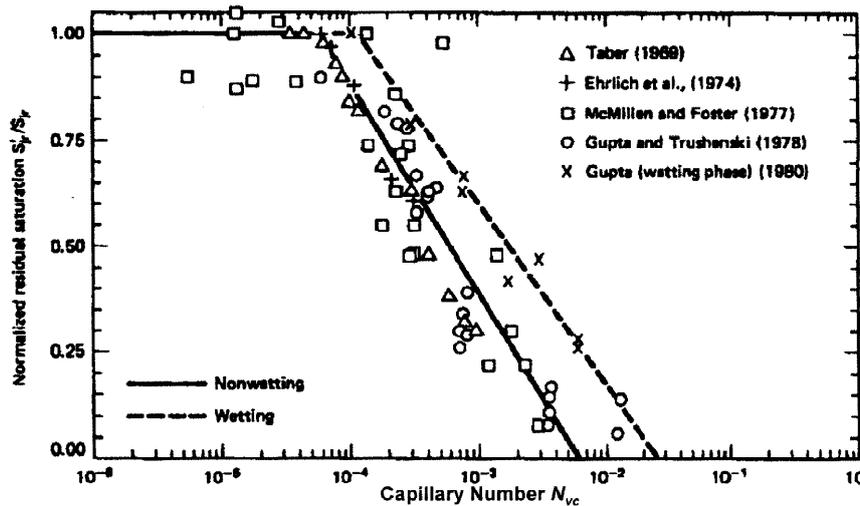

Figure 1 – Capillary desaturation curves [11]

The function of alkali, surfactant, and polymer during ASP

In EOR, flooding is based on the injection of water or another liquid, such as an alkaline solution, a surfactant solution etc., into the formation and driving the oil under the driving force of a pressure gradient.

ASP flooding [12] uses the benefits of the three flooding methods simultaneously (alkali-, surfactant-, and polymer-flood). Oil recovery mechanisms in alkali flooding are complicated. There are at least

eight postulated recovery mechanisms [13, 14], which include emulsification with entrainment, emulsification with entrapment, emulsification with coalescence, wet ability reversal, wet ability gradients, oil-phase swelling, disruption of rigid films, and low interfacial tensions. The existence of different mechanisms is ascribed to the chemical property of the crude oil and the reservoir rock. Various crude oils in different reservoir rocks show widely different behavior when they are subjected to alkali under different conditions such as temperature, salinity, hardness concentration, and pH. The commonly ac-

cepted mechanism states that the acidic components in the crude oil are the most important factor for alkali flooding. Furthermore, it states that the chemicals produced by *in situ* saponification increase oil recovery. The acid number of a crude oil is one of the most important parameters in alkali flooding and illustrates the amount of natural soap that can be produced by the addition of alkali. The alkali compounds [15, 16] include sodium hydroxide, sodium carbonate, sodium silicate, sodium phosphate, ammonium hydroxide etc.

Surfactants are considered to be good enhanced oil recovery agents since they can significantly lower the interfacial tension and alter wetting properties [8, 17-19]. However, the major limiting factor is price. Therefore, it is very important to reduce the surfactant consumption for EOR process and to use it in ASP. Surfactants are classified into four groups: anionic, cationic, nonionic, and amphoteric (or zwitter ionic) surfactants. Anionic surfactants, including soap, are negatively charged, and the counter ions are usually small cations. The reason for the use of anionic surfactants in ASP is their relatively low adsorption in sandstone and clays, their stability and their relatively cheap price. Because of high adsorption of positively charged surfactants on anionic surfaces of clays and sand, cationic surfactants are not popular choice for oil recovery in sandstone. However, there are some investigations performed on cationic surfactants in recent years for carbonate reservoirs. The main mechanism of cationic surfactant flooding is wet ability alteration and the formation of ion-pairs between the positively charged surfactant monomers and negatively charged adsorbed material, which consists of mainly carboxylic groups on the surface. The resulting desorption makes the rock surface more water-wet, and water will spontaneously imbibe into the matrix due to the capillary effect. As far as nonionic surfactants are concerned, the ether groups of nonionic surfactants form hydrogen bonds with water so that nonionic surfactants exhibit surfactant properties. These chemicals derive their polarity from having an oxygen-rich portion of the molecule at one end and a large organic portion at the other end. The oxygen component is usually derived from short polymers of ethylene oxide or propylene oxide. As in water, the oxygen provides a dense electron-rich atom that gives the entire molecule a local negative charge site that makes the whole molecule polar and able to participate in hydrogen bonding with water. Amphoteric surfactants

[20] may contain both positive and negative charges. These surfactants have not been tested in oil recovery. To have a successful commercial application using surfactants for oil recovery, the surfactant retention should be diminished. The retention mechanism of surfactants is attributed to adsorption, precipitation, ion exchange and phase trapping since the different mineralogy, including reservoir rocks, has different charges and properties. Furthermore, silica has a different isoelectric point in comparison with calcite, dolomite and clay, which have a positive charge on their surfaces at acidic pH. The electrical interaction between the charged solid surface and surfactant ions is the main cause of ionic surfactants adsorbing onto a solid and is explained by electrical double layer theory. For example, in hard brines, the divalent cationsreadily precipitate the surfactant as follows:

$$2R^- + M^{2+} \rightarrow MR_2 \downarrow$$
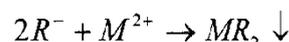
where R is the anionic surfactant. MR_2 is the surfactant-divalent cation complex that has a low solubility in brine.

Polymer is applied to change the mobility ratio to a favorable number since the injected fluid would not bypass the displaced fluid, i. e. crude oil in reservoir. Changing the properties of the crude oil or the permeability of the reservoir is not feasible from economic and technical points. Most mobility control methods change the properties of injected fluid. Polymer can significantly increase the apparent viscosity of the injected fluid. Foam is also a good mobility control method with water, surfactant and gas. Because low surfactant concentrations are used and much of the injected material is a gas, the cost of the chemical for foam can be much less than for the polymers. The mobility ratio will be lowered by using polymers which donot affect residual oil saturation with a few exceptions. But polymers greatly increase sweep efficiency. Two types of polymers, polyacrylamide and polysaccharide, are commonly used in enhanced oil recovery.

Numerical Simulation

Many simulation models have been developed to evaluate ASP process and direct the oil field applications of EOR techniques efficiently. Simulation techniques also minimize numbers and complexity of flooding experiments and help research-

ers to understand the characteristics of the ASP process. There has been much work simulating the ASP process by different companies to predict the EOR experiments and optimize reservoir performance. These programs use the solutions of the equations that govern multiphase fluid flow in porous media using finite difference techniques.

In 1978, a 1-D numerical simulator was developed by Pope and Nelson [21] to describe surfactant enhanced oil recovery and it has been extended to other chemical processes and to 3-D as UT-CHEM [22-24]. Furthermore, ECLIPSE, which is a commercial reservoir simulator, was developed by Schlumberger. Two other software programs, VIP® and Nexus®, were developed by Halliburton. There are other simulators such as CHEARS by Chevron, and Empower by ExxonMobil. However, UT-CHEM is the only model which considers natural soap as an additional surfactant [25]. A simple 1-D model is one of the most applied simulators; it illustrates the characteristics of the ASP process and is applicable to understanding and optimizing the process. A one-dimensional, two phase, multi-componental simulator has been applied to calculate the profiles and oil recovery as a function of process variables.

Design of ASP formulationMicroemulsion

Micro emulsion is a very important concept to design the formula of enhanced oil recovery. It is formed because of ultra-low interfacial tension. Phase behavior screening is an important parameter to observe the formation of micro emulsion and quickly evaluate favorable surfactant formulations. In 1954, Winsor [26] first described the phase behavior of micro emulsions for surfactant, oil and brine systems with different types and concentration of surfactants, co surfactants, oil, brine, alcohol, temperature, etc. The ternary phase diagram is a convenient tool for describing the micro emulsion phase behavior [8, 27] and shows the relationship between salinity changes and the phase behavior. Micro emulsions can be classified into three classes: lower-phase micro emulsion, upper phase micro emulsion and middle phase micro emulsion.

The main mechanism for formation of micro emulsions with ionic surfactants is derived from electrostatic forces. These forces will spontaneously change the curvature of the drops and produce the different types of micro emulsion systems. Furthermore, at low salinities, the micro emulsion is

formed as an oil-in-water micro emulsion with pure excess oil. Due to the difference between the density of this kind of microemulsionand the oil phase, this micro emulsion is formed below the oil phase, which is called "lower phase" microemulsion (named as Winsor type I, or type II(-). With increase of salinity, the size of the micro emulsion drop will increase and solubilization of oil will be augmented since the repulsion between the charged head groups decreases. If the salinities are very high, the electrostatic forces change the sign of the drop curvature, and water-in-oil micro emulsion forms. Since the formed micro emulsion is lighter than the water, which is pure excess phase and above the water phase, it is called an "upper phase" microemulsion (also named type II (+) or Winsor type II). However, at intermediate salinities, amicroemulsion is in equilibrium with both excess oil and brine. The micro emulsion is between the oil and brine phase, which is called "middle phase" micro emulsion (named type Ill, or Winsor type III). The micro emulsion contains almost all the surfactants in the system. Formation of this type of micro emulsion is important to design the ASP system for oil recovery because of its ultra-low interfacial tension. The phase structure of middle microemulsionis intricate and needs to be further investigated. Scriven (1976) suggested that the middle phase micro emulsion is a bicontinuous structure. Burauer S. et al developed theoretical models and some experimental observations to understand the bicontinuous micro emulsion system. Since both the oleic phase and aqueous phase are continuous, the interfacial tensions between the middle phase and either excess brine or excess oil are very low.

Phase Behavior and Interfacial Tension

Healy and Reed [27] first established an empirical correlation between the micro emulsion phase behavior and the interfacial tension (Fig. 2). They introduced solubilization ratios and described the corresponding behavior of the solubilization parameters and IFT with different salinity. In figure 2, σ_{mo} represents the IFT between the micro emulsion and the excess oil phase, and σ_{mw} represents the IFT between the micro emulsion and water phase. Figure 2 shows that σ_{mo} is high in the type I region and does not exist in the type II region. However, σ_{mw} does not exist in the type I region and σ_{mw} is high. In the type III region, both σ_{mo} and σ_{mw} arethe lowest values and are equal. The term

corresponding to this value is the optimum salinity [28]. The solubilization parameter V_o/V_s is defined as the volumetric ratio of solubilized oil to surfactant, and V_w/V_s is the water to surfactant ratio in the micro emulsion phase. Figure 2 shows that if V_o/V_s increases with salinity, V_w/V_s decreases with salinity. However, at optimum salinity, the amount of oil and brine solubilized in the surfactant phase are approximately equal. This is also another definition of optimum salinity. These two parameters are very important in designing the ASP flooding technique.
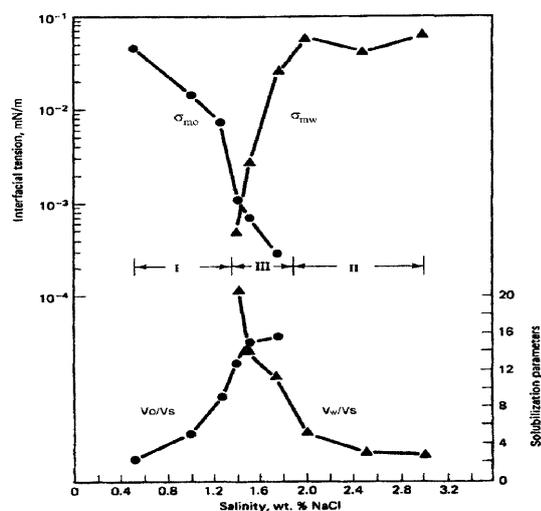
Figure 2 – Interfacial tension and solubilization parameter versus salinity [29]

As discussed in the section about the relationship between capillary number and interfacial tension, while interfacial tension is a low value, capillary number is large, and the residual oil saturation goes to zero. This is the main basis for designing the enhanced oil recovery formula. Healy and Reed [27, 30] proved that the optimum salinity was the salinity for maximum oil recovery by core flooding experiments. Clearly, one of the goals is to use the surfactant at the displacement front near optimum conditions in the ASP flooding. At this optimum salinity, the contact angles are equal. In 1979, Huh [31] developed a theoretical formula and described the relationship between solubilization ratio and IFT (equation 7). The IFT is inversely proportional to the square of the solubilization ratio, S. Based on Huh's equation [31], C=0.3 is a good approximation for most crude oils and micro emulsions.

$$\sigma = C/S^2 \qquad (7)$$

In 1979, Glinsmann [32] experimentally confirmed this relationship. Sometimes, it is difficult to measure the IFT between some crude oil and its lower phase micro emulsion. Through phase behavior observation and measurements of the solubilization ratios, the IFT of the oil / water / micro emulsion system can be estimated. It is very important to confirm a good formulation by considering both phase behavior and IFT measurement in ASP floods. Therefore, oil recovery is greatly enhanced by decreasing IFT, increasing the capillary number, enhancing the microscopic displacement efficiency, improving the mobility ratio, and increasing macroscopic sweeping efficiency. ASP flooding combines various mechanisms into a process.

Experimental evaluation approach

The results from phase behavior, IFT, adsorption and simulation helps to design ASP flooding experiments, which include a core flooding experiment. They can be used to prove those important mechanisms and provide the directions for the real field test.

IFT measurement methods [19] include capillary rise, Wilhelmy plate, Du NoUy Ring method, spinning drop, pendant/sessile drop, maximum bubble pressure method, etc. There are two methods which can be used extensively. Furthermore, pendant drop is usually applied to measure relatively high tension samples (above 1 mN/m). The pendant drop method is used to determine the interfacial tension based on geometric analysis of the interface of the drop and is performed on a drop of liquid surrounded by the other phase. But it is still very difficult to measure the tension that is less than 10^{-2} mN/m. A typical crude oil/brine interfacial tension is around 20-30 mN/m. Spinning drop [19] isa good fit for measuring the ultra- low tension system. In this method, two immiscible fluids are added in a capillary tube at the same time and rotated. Fluid A has different density from fluid B and is less dense than fluid B. Fluid A stays in the center of the capillary tube and forms an elongated drop through the centrifugal field generated by rotation forces. The geometry of the drop is related to the balance of the centrifugal force and interfacial tension force. In this force balance, the centrifugal force stretches the drop, while the IFT prevents this elongation. For a cylindrical shape drop that has a length at least four times greater than its radius, the following expression (equation 8) is often used to

calculate IFT, where σ is interfacial tension. Δρ stands for the density difference of the two fluids, while ω is a rotation rate. The radius of the less dense drop is r.

$$\sigma = \Delta\rho\omega^2 r^3/4 \qquad (8)$$

Phase behavior screening is a direct and simple way to predict the low IFT flooding formula as was discussed above. Type III or middle-phase micro emulsions exhibit the lowest IFT. For anionic surfactants, increasing the salinity, among other variables, causes the characteristic transition from Type I to Type III to Type II. Healy et al. presented the concept of optimum salinity as it applies to Type III micro emulsions. They observed the volumes of oil (V_o) and water (V_w) per unit volume of pure surfactant (V_s) in middle-phase micro emulsions and defined the optimum solubilization ratio (s*) as the intersection of plots of V_o/V_s and V_w/V_s as a function of salinity or other variables that affect the phase behavior. The intersection point represented a Type III micro emulsion with an optimal solubilization ratio (s*) and optimal salinity value.
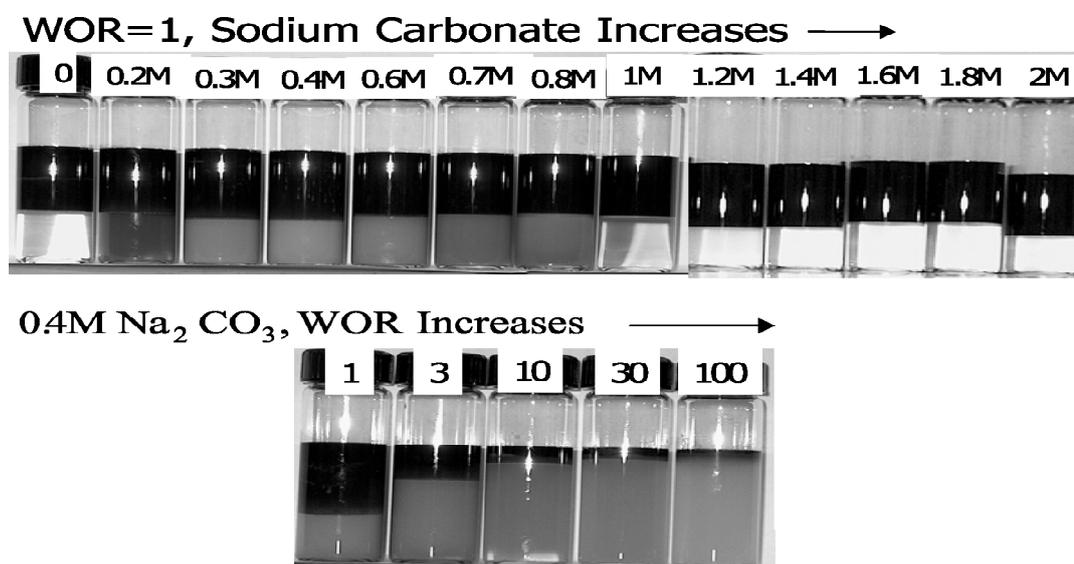

Figure 3 – Phase behavior of MY3 crude oil with 0. 2% (AM) TDA [33]

Core flood tests can be used to evaluate effects of alkali concentration, surfactant concentration, slug sizes, injection scheme, and potential use of chemical flooding for a field application. An ASP flooding system developed by Li etal [12] consists of1. 0% alkaline, 0. 5% nature mixed carboxyl ate surfactant (SDC), 1000 ppm polyacrylamide. The system that included nature mixed SDC was studied to examine phase behavior, interfacial tension and oil recovery. The ASP flooding results (Fig. 4) show high oil recovery, which is up to 26. 8%.

Survey of researches on ASP flooding

Most of researches on EOR are devoted either to one chemical component flooding such as alkali flooding, surfactant flooding, polymer flooding, or two chemical component flooding such as alkaline-surfactant (AS), alkaline-polymer (AP), surfactant-polymer flooding (SP)[34] that are effective strategy to increase oil recovery [35]. In this subchapter only ASP flooding consisting of more than two chemical components in the oil displacing formula is considered. Due to the synergetic effect and multiple functions of chemicals, the oil recovery of chemical combination flooding is higher than that of one or two component chemical flooding [36]. The contribution of alkaline (A), surfactant (S), polymer (P), and their combinations as AS, AP, SP to EOR was evaluated by authors [37]. For this a specially designed 2-D physical model was used and the dominant mechanism of enhanced heavy oil recovery was identified. Analysis of the seven 2-D sand pack flood tests shows that, for the heavy oil

tested, polymer flooding is an effective method to increase the final oil recovery, while alkalis and surfactant can help reduce the IFT, and, thus, increase the displacement efficiency. The combination of AS can reduce IFT to a much lower level, and yields a higher oil recovery than both alkaline-only and surfactant-only flooding. The combination of all three chemicals ASP yields the highest oil recovery.
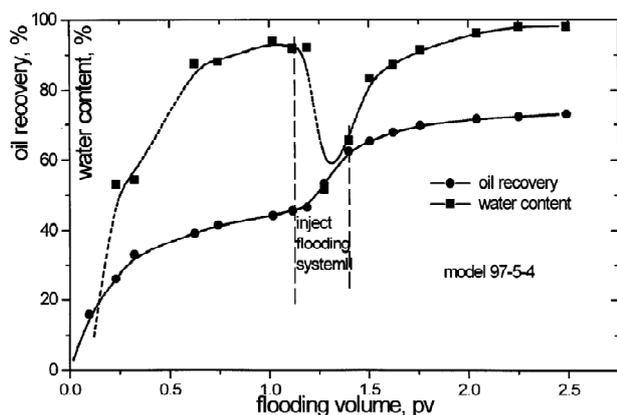

Figure 4 – Dynamic flooding process curve of system [12]

ASP flooding is complex and involves chemical reactions that depend on the oil composition, water composition, rock mineralogy, temperature, pH, etc. Authors [38] developed simplified ASP model and implemented it in a 3D chemical flooding reservoir simulator. The essence of the proposed model is that the reaction of acidic species at high pH generates soap and comprehensive phase behavior model for the mixture of soap and surfactant. Three ASP corefloods were modeled using simplified model and the proposed model can easily be implemented in any existing surfactant/polymer model. Simulation experiments were conducted to examine the effects of ASP on w/o [39] and stability o/w separation [40] in produced water from ASP flooding. The emulsion stability of water produced from ASP flooding was investigated by conducting settling experiments and measuring the oil–water interfacial properties [41]. The experimental results show that the addition of hydrolyzed polyacrylamide degrades the emulsion stability when its concentration is below 300 mg/L for the molecular weight $M_W = 1.2 \cdot 10^7$, and 800 mg/L for the $M_W = 3.0 \cdot 10^6$. But it enhances the emulsion stability when polymer concentrations are above those levels. At low polymer concentrations, flocculation induced by the polymer on oil droplets in the produced water is the dominant factor, while at high polymer concentrations the produced water viscosity plays an important role in the emulsion stability. The adsorption of surfactant on the oil–water interface increases the zeta potentials and decreases interfacial tension, and thus remarkably enhances the emulsion stability. Furthermore, the emulsion stability is enhanced gradually with the increase of NaOH concentration up to 300 mg/L due to the increase of zeta potentials and decrease of interfacial tension, and then weakened with the further increase of NaOH concentration, which is attributed to the decreased strength of the interfacial film.

Comprehensive research was devoted to determination of the impact of mineralogy and clays on the performance of ASP floods in sandstone formations [42]. Three flooding experiments (two single-phase and one two-phase flow) are carried to investigate the impact of active clays on permeability reduction and its reversibility, water chemistry changes and performance of ASP flooding.

Based on physico-chemical properties of polymer, surfactant, and alkali and their mutual interaction in solution, authors [43] recommended the following optimal composition of an ASP slug consisting of SDS: 0.1 wt. %, SDBS: 0.075 wt. %, polyacrylamide: 2000 ppm, and NaOH: 0.7 wt. %. Two sets of core-flooding experiments have been conducted using the designed ASP slug in a tri-axial core holder to measure the additional recovery of oil. The average additional oil recovery over conventional water flooding was found to be more than 20% of the original oil in place (OOIP).

A dilute SP flooding system has been designed and developed for Gudong oilfield with Shengli petroleum sulfonate (SLPS) as the primary ingredient [44]. The SP flooding formulation was finalized as 0.3% (w/w) SLPS + 0.1% (w/w) 1# + 0.15% polyacrylamide (PAM), in which 1#, the secondary surfactant, is able to enhance the interfacial activity of SLPS and the flooding efficiency of the system. The pilot field trial of the system started in June 2004 and finished in 2008 exhibited outstanding performance to improve oil production that had risen by 17.8×10^4 tons, with the oil-recovery increase by 6.4%. Studies have been done to examine the applicability of natural surfactant and polymer for enhanced oil recovery.

Authors [45] investigated interfacial and rheological properties of natural polymer – guar gum

and natural surfactant obtained from extracted soap nut shell. Based on the physicochemical properties of the surfactant and polymer solutions, optimum compositions were designed for flooding experiments. Three sets of experiments were performed to study enhanced oil recovery by injecting the same pore volume of polymer, SP, and ASP slug after brine flooding. Significantly higher additional recovery (~24% OOIP) was obtained by alkaline–surfactant–polymer flooding compared to the other two methods over water flooding (~50% OOIP).

The synergistic effects of NaOH, alkylbenzyl-sulfonate, and partially HPAM on the emulsification and destabilization of O/W crude oil emulsion produced by ASP flooding were studied [46]. The experimental results showed that the major factors governing the stability against phase separation of O/W ASP flooding produced fluid include the enhanced emulsification of produced fluid by alkaline, surfactant and HPAM, in which smaller oil droplets are generated, and the hindrance of alkaline and surfactant to oil droplet flocculation and coalescence.

The alkali consumption regularities for five kinds of minerals (kaolinite, grundite, chlorite, feldspar and quartz) in ASP and single component NaOH solution were studied [47]. It was found that alkali consumption is mainly caused by clay minerals and is 18.3% larger in average than matrix minerals. It was concluded that the main alkali consumption style in ASP system is the physical absorption; but for matrix minerals, the main alkali consumption style is the chemical reaction.

Alternative to conventional ASP flooding the chemical formulation using a new polymeric surfactant was suggested [48]. The polymeric surfactant used was poly(sodium methyl ester sulfonate) (PMES). Using 0.6 and 1 wt. % surfactant concentration, 16.2 and 20.7 % OOIP were recovered (Fig. 5). Such high oil recovery was due to the synergistic effect between polymeric surfactant and alkali to emulsify and mobilize the crude oil.

ASP methods to improve recovery of viscous oils were developed by authors [49].

The effectiveness of ASP system on EOR was tested with the help of sand-pack systems [50]. Re-

covery efficiencies vary 23–33 % of OOIP over the conventional water flooding. As seen from Table 1 additional recovery increases only marginally as concentration of PHPAM is changed from 1500 to 2500 ppm. Injection of polymer increases the sweep efficiency, and hence, oil recovery. After a certain concentration of polymer, the sweep efficiency approaches to its limiting value and thus only marginal additional recovery is observed.
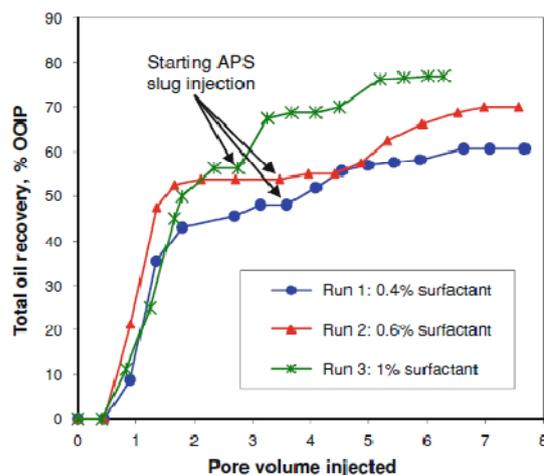

Figure 5 – Effect of various surfactant concentrations on oil recovery (Alkali 0.8 %)

Several mechanism viz., reduction IFT, emulsification of oil and water, solubilization of interfacial films, wet ability reversal, viscosity improvement, etc. are responsible for the EOR. Based on the experimental data and relative cost of different chemicals, concentration range of alkali (0.7–1.0 wt. %), polymer (1500–2500 ppm) and surfactant (0.2 wt. %) have been recommended for successful ASP flooding.

In EOR simulation model, two methods, polymer and SP floods, were compared [51]. The recovery factory for each case can be seen in Table 2. The incremental value displays the incremental recovery based on the adjusted water flood. The optimum polymer flood has a recovery contribution of 8.80%. The optimum surfactant-polymer process has another 2. 49% incremental recovery based on polymer flood.

Table 1 – Recovery of oil by ASP flooding with varying concentration of polymer

Expt. No.	Porosity (%)	Permeability, k (darcy)		Design of chemical slug for flooding	Recovery of oil after water flooding at 95% water cut (%OOIP)	Additional recovery (%OOIP)
		k_w ($S_w=1$)	k_0 (S_{wi})			
S6	37.265	1.144	0.217	0.3 PV (0.5% NaOH+0.1% SDS+1500 ppm PHPAM) + 0. 2 PV 1.5 ppm buffer + chase water	50.2	23.69
S7	36.805	1.145	0.218	0.3 PV (0.5% NaOH+0. 1% SDS + 2000 ppm PHPAM) + 0.2 PV 2.0 ppm buffer + chase water	52.8	23.5
S8	37.265	1.143	0.217	0.3 PV (0.5% NaOH + 0.1% SDS + 2500 ppm PHPAM) + 0.2 PV 2. 5 ppm buffer + chase water	52.9	24.2

Table 2 -Recovery Summary of different EOR Methods

Method	Polymer			Surfactant -polymer	
Simulation case	4 million	6 million	9 million	Process 1	Process 2
Ultimate recovery (%)	58.21	60.78	59.13	63.27	62.84
Incremental value of OOIP (%)	6.23	8.80	7.15	11.29	10.86

The main technological problems occurred in the application of chemical combination flooding are: 1) to develop high-performance, low-cost surfactants for chemical combination flooding; 2) to develop new salt-tolerance, temperature-resistance polymers and surfactants; 3) to improve chemical combination flooding supporting technology in field tests and application; 4) to develop monitoring, tracking adjustment and optimizing technology in chemical combination flooding field tests.

ASP project performance

Two process units, which are water treatment and ASP preparation, are involved in using facilities for an ASP project. The ASP unit includes three subunits of alkali, surfactant, and polymer. Water is required in treatment for fullcompatibilty with the ASP chemicals. Ion exchange resin for water treatment is applied to meet the need of water softening, which isless than about 30000 ppm of total dissolved solid (TDS) content.

The West Kiehl ASP project [53] was considered as the first ASP project. This first alkaline-surfactant-polymer project was initiated in September 1987 in Minnelusa, Wyoming. The oil recovery was up to 23% OOIP. There have been performed many ASP technologies in the Daqing Field [54-57], Peoples Republic of China. Daqing is the largest oilfield in China. The results from all ASP projectsreported incremental recoveries of 20% OOIP or greater. In 1994, the first tertiary ASP project was performed in China. This test covered four injection wells, nine production wells, and a 5.5-acre pilot in the Saertu Sand. The ASP formula includes 1.25 wt. % Na_2CO_3 (alkali) plus 0.3 wt. % active Petro step B-100 (surfactant) plus 1200 mg/L Alco flood 1275 (polymer). Oil cuts reached a peak value of 48%. Oil rate and incremental oil respectively, are 61 m^3/day and 33,000 m^3or 31% OOIP. The ASP pilot test in Karamay EZ district, China [58] was performed starting on August 21st, 1995 and showed 24% OOIP incremental recovery in the whole test area. More ASP flooding tests have been applied in other oilfields of China. ASP field projects have been conducted in Canada and India. Table 3 summarizes the performance of some of the ASP projects worldwide.

Table 3 – ASP field tests

Project	Start Date	Area(Acre)	%OOIP	Reference
West Kiehl, Wyoming	1987	106	34. 4	53
Cambridge, Wyoming	1993	72	26. 8	59
David, Alberta	1986	252	21	59
Daqing, China	1994	8. 4	31	54, 60
Gudong, China	1992	766	29. 4	61
Karamay, China	1996	766	24	54,58
Viraj, India	2002	68	24	62
Tanner Field, WY	2000	44	44	63
La Salina Field, Venezuela	2001	1,445	24. 6	64

Conclusion

ASP technology has advantages including surfactants, alkali, and polymers with mobility control chemical (polymer). An alkaline-surfactant-polymer flooding technique has proved from oil field tests more than 20 % OOIP and has been successful in three completed projects in North America as well as several projects in China. ASP flooding technique has shown to be an economically viable technology in comparison with water floods. The above described significant performance of ASP technology is the results of the combined factors: reservoir engineering and geologic studies, laboratory chemical system design, numerical simulation, facilities design, and ongoing monitoring.

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