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ASP Flooding Produced Water Management: Evaluation, Disposal and Reuse

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Abstract

Alkali/surfactant/polymer (ASP) flooding technology has become an important way to enhance the oil recovery and improve the recoverable reserves. However, in the large-scale application, the disposal and reuse of ASP produced water meet lots of difficulties and challenges, especially with the water cut rising of the benefited oil wells and the appearance of polymer, alkali and surfactant in sequence in produced liquid. Many traditional disposal methods are suffering double restriction of purifying effect and economical efficiency, also, the discharge of the disposed water is faced with a variety of pressure, such as facilities pollution, healthy and environmental threat. Therefore, environmental friendly disposal and beneficial reuse of produced water have become one of the technical bottlenecks for the promotion of ASP flooding. A laboratory investigation of evaluating the microcosmic emulsification properties of ASP flooding produced water was carried out recently. A combined disposal process for the water was presented and assessed. The feasibility of produced water reuse for preparing polymer solution during the chemical flooding oilfield development at high water-cut stage was validated.

The results show that there are surplus negative charges on ASP flooding produced water interface. The oil droplet size in the water diminishes with the increase of the chemicals, and particles are easily absorbed on oil-water interface to further prevent the coalescence of oil droplets. The sludge accumulation was decreased more than 70.0% due to the physical comprehensive effects of the combined disposal process including sedimentation with aeration, lateral flow coalescence, dissolved air flotation and micro-flocculation suspended sludge blanket filtration. The power and agent expense was reduced 60.0% and secondary pollution was decreased remarkably. The produced water after disposal could not only meet the re-injection standard of high permeability reservoir, but also can be reused to preparing polymer solution, and the viscosity loss control ability is desirable. The treatment option presented in this paper would contribute more to establishing a health, safety and environment (HSE) system.

Introduction

As other chemical flooding enhanced oil recovery (EOR) technologies, alkali/surfactant/polymer (ASP) flooding's role is primarily one of extracting the last technically extractable drop of oil from the reservoir

while extending the economic life of the abundant mature oil fields¹. The technique has been developed on the basis of the synergistic effect of alkali-flooding, surfactant-flooding, and polymer-flooding in the 1980s². In this technique, the benefits of the three displacement methods are simultaneously played, macroscopic sweeping coefficient and microscopic displacing efficiency are enhanced. Apparently, the low crude oil prices after 1985 have discouraged the application of ASP in larger fields³. Today, however, chemical flooding, in particular ASP flooding has attracted remarkable interests because of high crude oil prices and the necessity to stabilize production levels from a maturing field base, it is receiving renewed attention. Up to 2012, Daqing Oilfield (China) was the first to realize industrialization promotion of ASP flooding throughout the world. The production practice shows that EOR of ASP flooding recovery is more than 5–8% original oil in place (OOIP) over polymer flooding⁴. In 2013, the production of ASP flooding in Daqing Oilfield approached to 8.2 million barrels (bbl). In the world, much intensive studies have been done on ASP flooding recently, some important accomplishments were achieved and a solid foundation for the extension of this displacement technique to practical operation in oilfields was established^{5,6}. But including produced water intractable emulsification, scaling appearance on the wellbore, downhole equipment and surface equipment, and the issues of facing large-scale produced water governance pressure are still the technical bottlenecks for the promotion of ASP flooding^{7,8,9}.

Though emulsification is a complex process, it is widely existed in oilfield ASP flooding. As widely understood, emulsification process is influenced by the local shear field and the physical and interfacial properties of the phases in contact with each other. All the time, emulsion quality has been defined in terms of the droplet size and droplet size distribution which depend on the hydrodynamic conditions existing in the production facilities as well as the physiochemical nature of the interface between the continuous phase and disperse phase^{10,11}. The chemicals appeared in ASP flooding produced water are act as emulsifier, playing an important role for emulsification processes. The chemical adsorbed on the droplet interface is very fast and it precedes droplet deformation, breakage and collision, make the stronger stability of oil-water emulsion¹². Overall, the chemical demulsification method is by far the most widely used in the ASP flooding industry, both from an technical and effective point of view, but high budgets reduction and pursuit of HSE for a green field development are still can't be ignored^{13,14,15}.

Even though the produced water could be direct discharged after deep disposal, it can also lead to many operational and environmental problems. Therefore, particularly in high water-cut stage oilfield development, the options, such as produced water re-injection (PWRI) and reuse in boiler, can be put as an effective way to get rid of the problems of economy, technique and environment^{16,17}. In the early 1980s, due to frequent scarce supplies of available fresh water in the principal oil production areas of western Canada, several operators of in-situ recovery projects were devoted in reusing produced water for steam generation in their commercial projects¹⁸. With the gradually formed green field development idea, interest of produced water reuse has been stimulated by environmental pressure to explore alternatives for produced water disposal by re-injection. In other words, development and implementation of advanced technology to purify produced water has been environmentally driven. To date, a number of methods are available to treat oilfield produced water to prepare it for reuse^{19,20,21}. Still, reliable, proven technical method also is key of large-scale popularization and application.

This paper emphasizes the microcosmic emulsification properties of ASP flooding produced water. Presentation of an environmental friendly combined process of removing the oil and suspended solids in produced water, which is mainly by physical comprehensive action, combats lots of operational and economical problems such as re-emulsification and secondary pollution. Under the optimized operating parameters, such as aeration rate, dissolved-air pressure, reflux ratio and filtering velocity, application effect was demonstrated and practiced. Laboratory scaling experiments were conducted to identify the properties of water quality after disposal and polymer solution prepared by the water. The application of PWRI in high permeability reservoir was evaluated. The variation and control method of viscosity loss were also established and simulated. Finally the affect of viscosity loss and the control ability of reuse for

Table 1—Oil-water interface Zeta potential of ASP flooding produced water with different appeared chemical concentrations (average appeared polymer concentration is 800mg/L)

Zeta potential average value, mV	Appeared surfactant concentration, mg/L				
	<20	20~80	80~150	150~220	220~300
Appeared alkali concentration, mg/L	<150	-40.15	-57.35	-62.19	-65.40
	150~350	-38.74	-54.29	-61.70	-65.11
	350~600	-35.31	-53.71	-56.29	-61.03
	600~900	-34.06	-51.22	-54.46	-57.92
	900~1300	-31.78	-49.97	-52.37	-57.14
					-56.69

preparing polymer solution with the disposed ASP flooding produced water by the environmental friendly method were studied, and the reuse feasibility and mechanisms were explained. The results would contribute to saving fresh water resource, avoiding the discharge of waste water during oilfield development at high water-cut stage, and establishing a new HSE system.

Microcosmic emulsification properties of ASP flooding produced water

Diffused double layer Zeta potential on oil-water interface

The produced water used for Zeta potential measurement were sampled from the wellhead of production well in strong base (NaOH) ASP flooding area in Daqing Oilfield. In the development of this area, the injection concentrations of chemical slug were of the order of 1.2%(wt) alkali (NaOH), 0.3%(wt) surfactant (major component of alkylbenzene sulphonate) and 1800mg/L polymer (the molecular weight of 2500×10^4). The average salinity of the produced water is above 6000mg/L, the oil content is over 1000mg/L and the median diameter of oil droplet is about 20 μm . The production wells with about 800mg/L appeared polymer concentration in produced water were screened. Then, according to the appeared concentration distribution of alkali, surfactant in produced water, the samples were divided into 25 kinds as shown in Table 1. The emulsified water in the lower layer were taken out respectively, and by means of nanoparticle size and Zeta potential analyzer (MICROTRAC, Nanotrac wave), the Zeta potential of oil-water interface under 40°C was measured. The polymer concentration was determined by starch-cadmium iodide method, alkali concentration was characterized by acid-base titration, and the surfactant concentration was measured by two-phase titration method with the methylene blue-methyl orange as indicator.

Table 1 indicates that there are surplus negative charges on different ASP flooding produced water interfaces, the diffused double layer is existed on oil droplet surface and Zeta potential value is lower than -30mV. With the increase of alkali concentration, because of the electrostatic repulsion between ionized contra-ion of alkali and original contra-ion of diffusion layer, some contra-ions are extruded into adsorbed layer. Then the thickness of diffusion layer is thinned, making the Zeta potential value raised in different degrees. With the increase of surfactant concentration, due to the adsorption of surfactant molecules on oil-water interface, the electronegativity of the interface is strengthened, the electrostatic repulsive-force of oil droplets is enhanced, gather and coalescence of the drops are restrained, and the corresponding Zeta potential values are decreased significantly. However, when the surfactant concentration exceeds 150mg/L, in different alkali concentrations, the absorption get saturated gradually and the variation of Zeta potential value is stable. This result is in agreement with the strong emulsion stability of ASP flooding produced water.

Oil-water dynamic interfacial tension

The produced water with different appeared chemical concentrations were sampled from the same production wellhead in strong base ASP flooding area in the oilfield. In the experiment, settle the water at 40°C, remove the suspended solid by sedimentation, transfer the emulsified water, then the oil-water

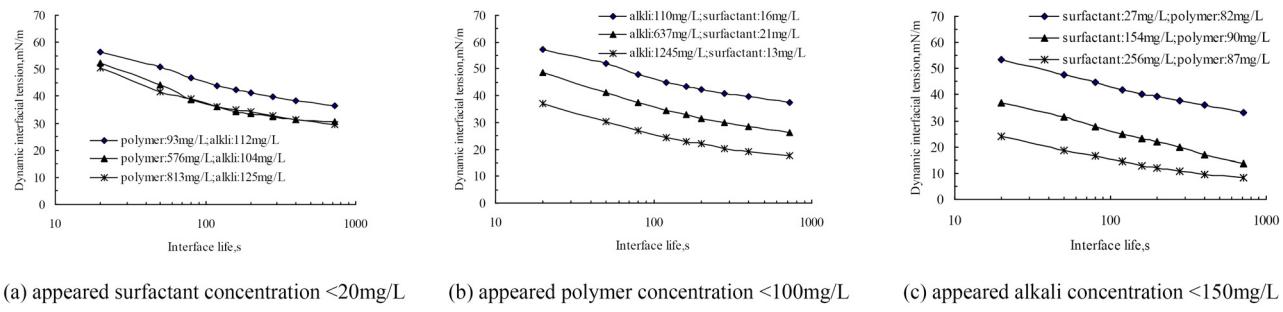


Figure 1—Influence of interface life on oil-water dynamic interfacial tension

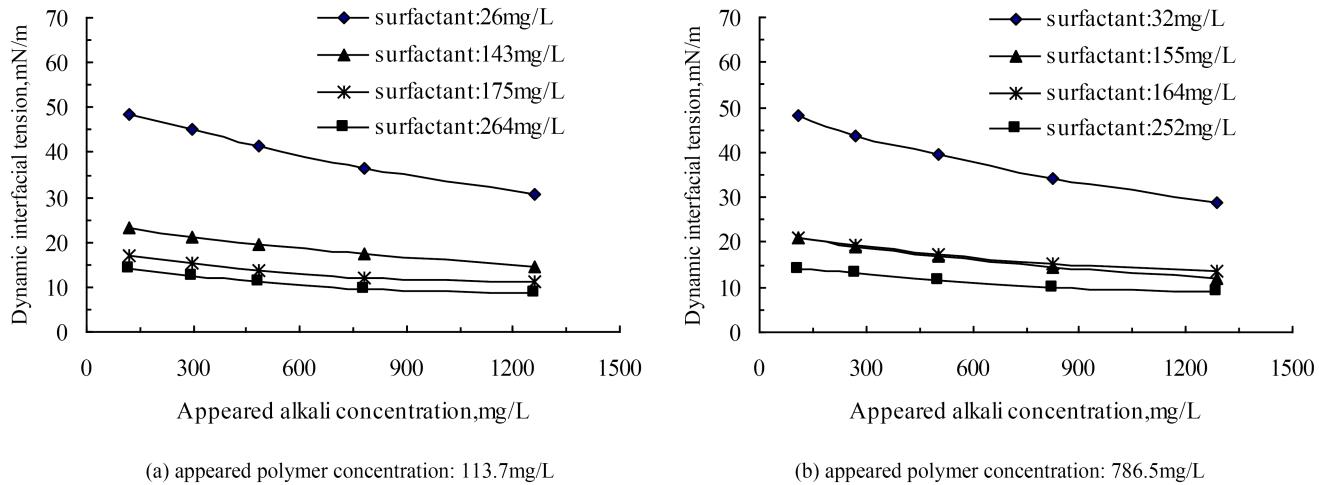


Figure 2—Influence of appeared chemical concentrations on oil-water dynamic interfacial tension

dynamic interfacial tension is measured at 40°C by interface tensiometer (Krüss DVT-50) with the titration volume method.

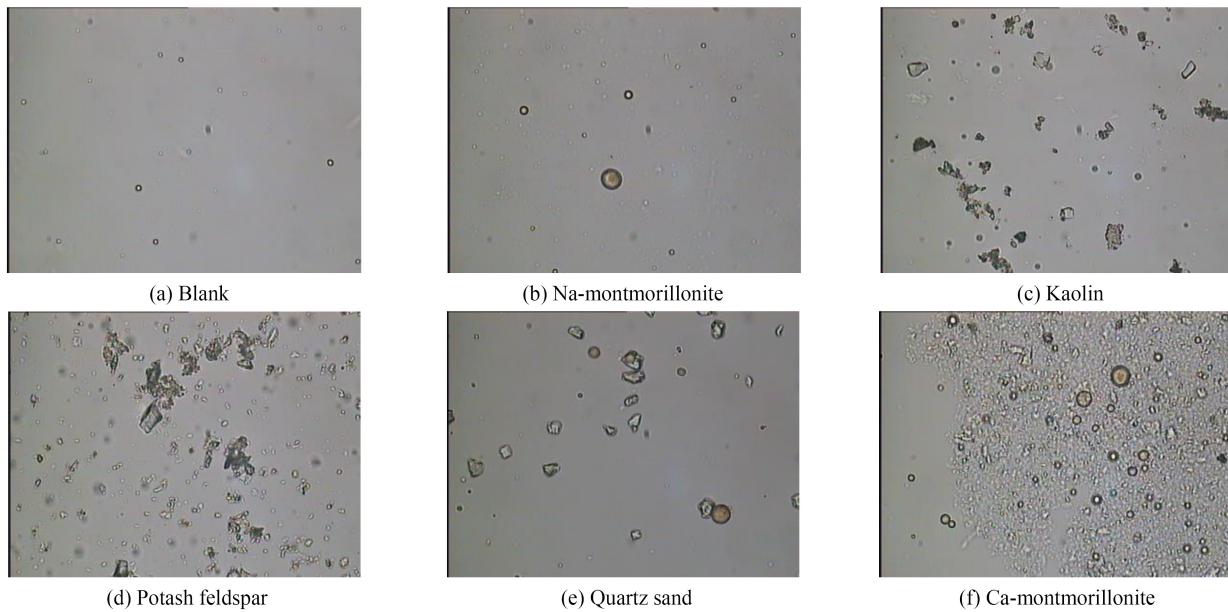
As shown in Fig.1, under different appeared chemical concentrations, oil-water dynamic interfacial tension of ASP flooding produced water decreases with the increase of the interface life, because as the interface life increasing, the oil-water interface further tends to be balanced, and the dynamic interfacial tension further tends to be equilibrium interfacial tension. Fig.2 shows that, among the chemicals, the influences of alkali and surfactant on oil-water interfacial tension are the most significant. The maximum decreasing amplitude of dynamic interfacial tension reaches 42.5% as the alkali concentration increases to 1300mg/L. The dynamic interfacial tension decreases from 50mN/m to 10mN/m sharply when the surfactant concentration is in the range of 0–150mg/L. Polymer causes the water phase viscosity increase, which made the dynamic interfacial tension decreases slightly. This reflect that saponification could be happened between alkali and organic acids of crude oil colloids and asphaltenes, such as carboxylic acid and naphthenic acid. The surface active substances like aliphatic acid and naphthenic acid could be generated, and then adsorb on oil-water interface with the appeared surfactant, making the interfacial tension decreases remarkably. Consequently, under the same phase interface area, thermodynamic stability of emulsion is strengthened with the decrease of interfacial energy.

Influence of solid phase particles on oil droplets coalescence

The produced water with 3 different appeared chemical concentrations were sampled from the production wellhead in the same area in the oilfield. Solid phase particles of Na-montmorillonite (average particle diameter is 2 μ m), kaolin (average particle diameter is 3 μ m), potash feldspar (average particle diameter is 3 μ m), quartz sand (average particle diameter is 2.5 μ m) and Ca-montmorillonite (average particle diameter is 2 μ m) were put into the water respectively with the mass concentration of 0.5%. Oscillate and

Table 2—Influence of solid phase particles on emulsified oil content in ASP flooding produced water

Solid phase particle types	Emulsified oil content, mg/L		
	Sample 1	Sample 2	Sample 3
Blank	875.2	1046.5	1213.4
Na-montmorillonite	886.7	1102.7	1194.6
Kaolin	913.5	1059.4	1240.7
Potash feldspar	894.1	997.8	1175.3
Quartz sand	968.4	1203.4	1390.8
Ca-montmorillonite	1017.5	1258.1	1427.5

**Figure 3—Micrograph of the adsorption behavior of solid phase particles on oil droplet surface**

mix the solutions in test tubes, then settle for 8h at 40°C. Emulsified oil content in the lower water was measured by spectrophotometer (PerkinElmer, Lambda35). Put the bottom deposition on the slide of hot-cold stage (Linkam, LTSE420), an optical microscope (Xiamen Hyhoo Imp. & Exp. Co., Ltd., XSZ-106) equipped with a digital camera was used to observe the adsorption behavior of solid phase particles on oil droplets surface at 40°C, then compared the properties with the raw produced water which is without solid phase particles.

As shown in **Table 2**, for the same sample of produced water, the emulsified oil content after sedimentation is much higher with the exist of quartz sand and Ca-montmorillonite. This reveal that the solid phase particles like quartz sand and Ca-montmorillonite would prevent the coalescence of oil droplets and deteriorate the oil-water separation effect.

In the ASP flooding produced water, the presence of particles at the oil-water interface would suppress drop-drop coalescence and increase emulsion stability. The micrographs illustrate that, compared with Na-montmorillonite, kaolin and potash feldspar, the mineral particles of quartz sand and Ca-montmorillonite are easier adsorbed on the oil-water interfaces. This is because the particles are much easier charged, providing repulsive interactions of droplets, and can bridge across neighboring emulsion drops. In addition, they can impart enhanced interfacial viscosity that retards the thinning of an intervening liquid layer as the droplets approach each other. The absorption and insertion between solid phase particles and oil droplets would cause the formation of aggregations in different shapes. The density

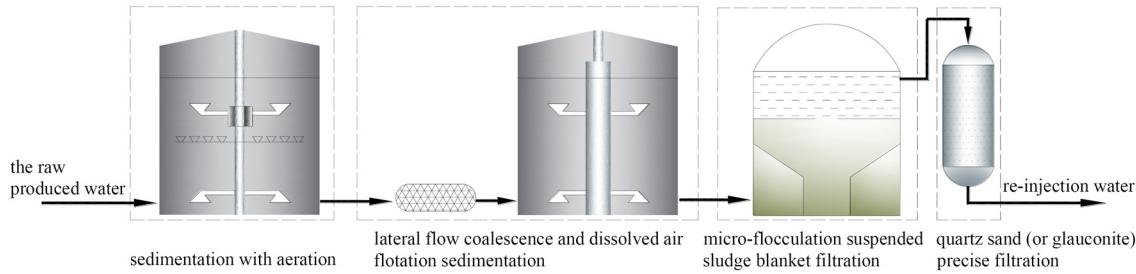


Figure 4—Schematic illustration of the ASP flooding produced water disposal process

difference between these aggregations and water is less than that between pure suspended solid and water. So based on the Stokes law²², we can defined:

$$V_s = \frac{d_s^2 g (\rho_s - \rho_w)}{18 \mu_w} \quad (1)$$

Where V_s is sedimentation velocity, ρ_s is suspended particle density, ρ_w is water phase density, d_s is suspended particle diameter, μ_w is water phase viscosity and g is acceleration of gravity.

The formation of aggregations prevent the rising, collision and coalescence of oil droplets, sedimentation velocity of the droplets is also lower than that of pure suspended solid particles. Assuming these particles are spherical particles, the energy E required to detach a particle from oil-water interface into either bulk phase can be given by:

$$E = \pi r^2 \sigma (1 - |\cos \theta|)^2 \quad (2)$$

Where r is the particle radius, σ is the oil-water interfacial tension, and θ is the contact angle through either phase.

This is in agreement with ASP flooding produced water emulsified oil content data obtained under varying process conditions. Apparently, once a particle is in the interface it will not detach spontaneously, which reflect strong emulsion stability. Also, it proves that the influence of scaling mineral in ASP flooding on the decrease of oil-water separation efficiency can not be ignored.

Disposal method of ASP flooding produced water

Combined disposal process

In the previous article²³, we investigated the effects of aeration rate, sedimentation time, reflux ratio, dissolved-air pressure, filtering velocity on oil-water separation performance, and a physical comprehensive method to dispose the ASP flooding produced water was determined. As shown in Fig. 4, the raw produced water would be disposed by sedimentation unit with aeration, lateral flow coalescence unit, dissolved air flotation unit, and micro-flocculation suspended sludge blanket filtration unit in sequence. Furthermore, a conventional precise filtration unit with quartz sand (or glauconite) as filter material was added after the micro-flocculation suspended sludge filtration unit, which made the oil droplets, suspended solids and chemicals removed intensively. In this process, the large-close flocs are formed by adding flocculant into the micro-flocculation suspended sludge filtration unit only, and there is no other water treatment agent being added, so the healthy and environmental challenges during chemical flooding EOR process can be addressed by this environmental friendly method.

Process principle

For the sedimentation unit with aeration, when the raw ASP flooding produced water is pumped into, lots of bubbles would release from the releasers to mix with the tight emulsified water by aeration equipment. The oxidation effect of air bubbles caused by aeration process could reduce some organic materials in the water and decrease the viscosity. Also, the emulsified oil droplets could float to surface layer easily with

air bubbles and then removed easier. As a horizontal oil removal equipment, the polypropylene was installed as orthometric trapezoidal plate form, therefore, the larger size particles can be intercepted, and the small size oil droplets and suspended particles would also collide, gather and attach on coalescence plates of lateral flow coalescence unit. Then, when the produced water enter into dissolved air flotation unit, due to the micro-bubbles with $20\sim40\mu\text{m}$ diameter released from dissolved air pump, some pollutants would lose stability and break down into new suspended solids because of the oxidation-reduction effect of the floating low density bubbles-flock. So, with the obtained apparent separation effect, the oil removal efficiency is better than suspended solids.

The suspended sludge blanket has lots of effects, such as adsorption, filtration, electrical neutralization and net intercepting, and in the micro-flocculation suspended sludge blanket filtration unit, under the appropriate filtering velocity, these effects would cooperate with the flocculant to flocculate and enlarge the small size particles in produced water. Then, the produced water would be purified because the floated impurities are intercepted by the sludge blanket, and the head loss of the sludge blanket is increased due to the storage of the floated impurities. In the whole process, flocculation is the main form of adsorption. The precise filtration unit with quartz sand (or glauconite) as filter material plays a role of mechanical filter, the flocculated particles, oil particles, suspended solids, microorganisms and colloidal solids would be intercepted again, which would further improve the disposal effect.

Operation parameters and engineering application effects

In this combined disposal process, the obtained removal rates of oil and suspended solids are more than 40% by sedimentation with aeration for 6–8 hours, where the aeration rate should be increased until the dissolved oxygen (DO) concentration reached 6mg/L. In dissolved air flotation unit, the reflux ratio of about 40% and the dissolved-air pressure of about 60 psi are the most appropriate operation parameters for ASP flooding produced water. The dosage of flocculant in micro-flocculation suspended sludge blanket filtration unit is depended on its effect, but the best filtering velocity in sludge filter layer which is formed by flocculation, adsorption and interception is 0.0014m/s.

Under these conditions, the combined disposal process which is mainly by physical comprehensive action was engineering designed and applied in a water disposal station in one of the ASP flooding production areas of Daqing Sabei Oilfield. The operation practice shows the oil droplets and suspended solids were removed effectively, the concentrations of chemicals in the water after disposal were observably reduced, the particle size distribution in the water was decreased in both number and dimension, and a low Zeta potential was achieved. Compared with the previous polymer flooding produced water sedimentation and filtration disposal process, power and agent expense was reduced 60.0%, operating cost was saved, the sludge amount of the ASP flooding produced water was decreased more than 70.0%, re-emulsification was avoided, and secondary pollution was decreased drastically.

Reuse method of ASP flooding produced water

In the oilfield produced water treatment option, there are many technologies and now with the ever tightening discharge limits around the world, there appears to be a glut of new technologies appearing to achieve the mandate of zero discharge into the environment^{24,25,26,27}. However, as the ASP produced water is with complex compositions and strong emulsion stability, the adaptation of many technologies would face the challenges of purifying effect, secondary pollution and economical justification. The water re-injection in-situ after disposal in high permeability reservoir water flooding development, or preparing polymer solution in-situ during polymer flooding and ASP flooding are the effective methods of recycle and reuse with zero discharge.

Re-injection of high permeability reservoir

Experimental materials The cylindrical natural cores used for re-injection feasibility evaluation were sampled from the high permeability reservoir of Sa II horizon with 1048.1~1080.6m depth in Daqing

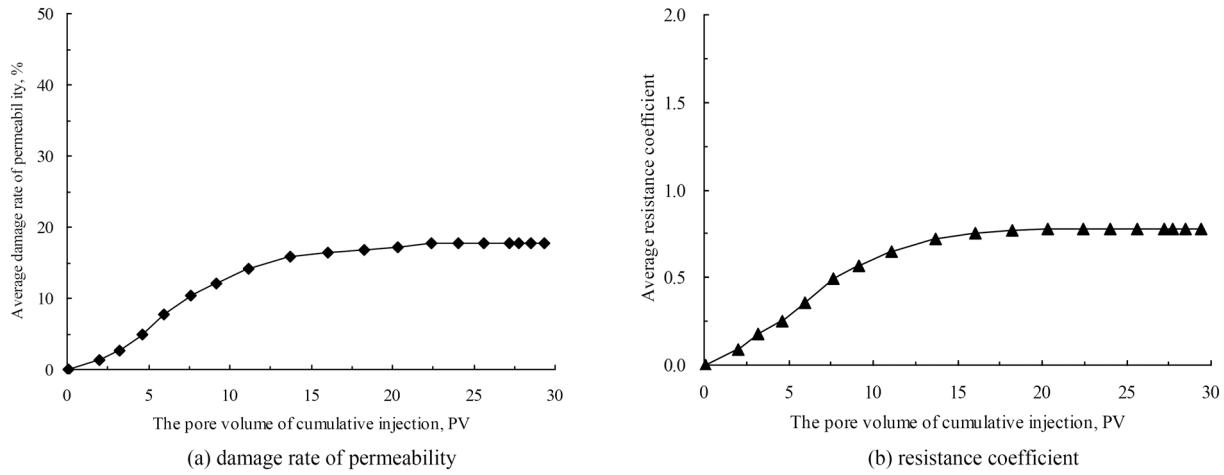


Figure 5—The variation of permeability and resistance coefficient of the reservoir re-injected with ASP flooding produced water

Oilfield, with a diameter of about 25mm, a length of about 80mm and the average air permeability of $1.2\mu\text{m}^2$. Simulated formation water was artificial prepared with the salinity of 6778mg/L. ASP flooding produced water was disposed by the above-mentioned combined process which is mainly by physical comprehensive action. The oil and suspended solid contents of the water after disposal were both lower than 20mg/L, median particle diameter was less than 5 microns, the number of sulfate reducing bacteria (SRB) was less than 100 ind/mL, and the chemical concentrations were lower than 100mg/L.

Experimental methods and principle The natural cores were extracted for about 72h by compound solvent (benzene/alcohol=3:1), and dried at a temperature of 105°C. Air in the cores were pumped out and the cores were saturated with the simulated formation water, then the effective permeability were measured. Afterwards, the disposed ASP flooding produced water was injected into with a constant flow to make the pressure stabilized and the permeability of the cores with different degrees of pollution were continuously measured again. Then, the damage rate of permeability and the resistance coefficient of the re-injection could be determined, and the law of oil reservoir pollution brought by re-injection was established.

$$\eta = \frac{K_e - K_{ri}}{K_e} \times 100\% \quad (3)$$

Where η is damage rate of permeability (%), K_e is core effective permeability (μm^2), K_{ri} is core permeability during produced water re-injection at any time (μm^2).

$$RF = \frac{(\Delta P)_{ri}}{(\Delta P)_e} \quad (4)$$

Where RF is resistance coefficient, $(\Delta P)_e$ is pressure drop of the cores when formation water flowed though (Pa), $(\Delta P)_{ri}$ is pressure drop of the cores when produced water re-injection (Pa).

Simultaneously, the injection face of the core was sliced before and after re-injection with the ASP produced water, then the variation of pore structure could be observed by scanning electron microscope (Hitach, S3400N). The feasibility of re-injecting the ASP flooding produced water was further examined.

Experimental results and analysis As shown in Fig.5, the average damage rate of ASP flooding produced water re-injected in high permeability reservoir is less than 20%, the average resistance coefficient of the re-injection is within 0.8 and it tends to be stable when the cumulative injection reached about 10 pore volume (PV). This seepage behavior are attributed to the residual oil droplets, suspended solid and polymer of ASP flooding produced water disposed by the combined process. At the same time,

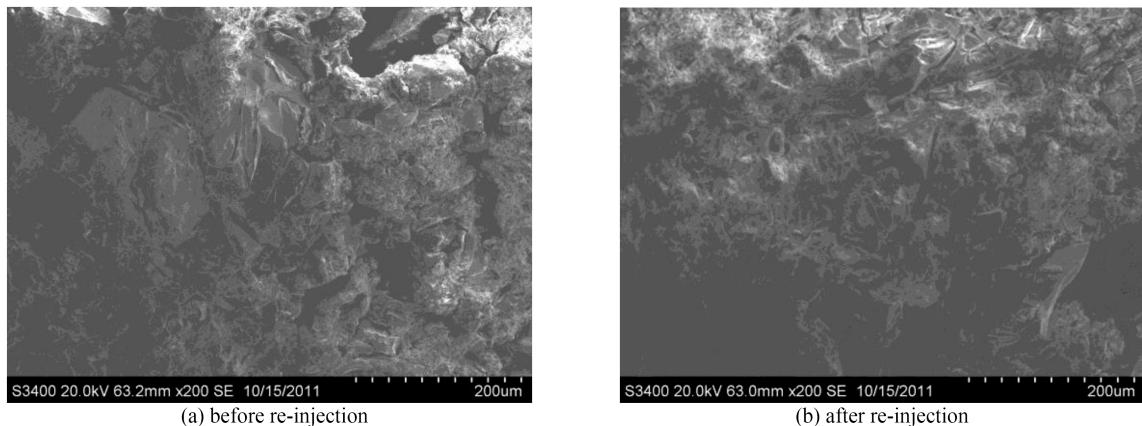


Figure 6—The scanning pictures of core slices before and after re-injected with ASP flooding produced water (amplification factor: 200)

the expansion of clay mineral in reservoir during re-injection and the inevitable consequence of velocity sensitivity effect caused by particle migration could not be excluded.

The microcosmic pore structure of the cores reveal that, the sharpness of mineral rock decreases in a certain degree after the ASP produced water cumulative injection reached at 30PV. But the morphology of minerals are still visible and there are no obvious differences in pore connectivity. The results indicate that the re-injection of high permeability reservoir with ASP produced water disposed by the combined process would not bring irreversible physical clogging and pollutions.

Preparing of polymer solution

Experimental materials and methods The polymer, with the relative molecular weight of 1900×10^4 and a hydrolysis degree of about 25%, was employed in the reuse experiment. The water used to prepare the polymer solution was the Daqing Oilfield ASP flooding produced water disposed by the above-mentioned combined process. Chemical oxygen demand (COD) of the water was 580mg/L (obtained by potassium dichromate method) and the DO concentration was lower than 1.5mg/L. In order to control the viscosity of the prepared polymer solution and achieve the successful reuse, aeration on the disposed water is necessary before the preparation, because the aeration oxidation can contribute to the sterilization and efficient removal of reducing substances. Then, the influences of water flow rate and distance on this reuse method are simulated in sequence.

Experimental device and setup The aeration-loop unit equipment which is used for the re-aeration of the disposed ASP flooding produced water and simulation of the flow, as demonstrated in Fig. 7, is made up of air compressor, water gathering tank, closed loop (the inner diameter is 1.5 inch), variable frequency circulating pump, flowmeter and storage water tank. The water gathering tank is divided into gas dissolved room and gas released room by microporous baffle. In the operation, the disposed produced water was put into water gathering tank first, and then the air compressor was opened to realize re-aeration. The reducing substances of the water would be removed by controlling the processing pressure and time, and the bacteria were also killed in different degrees. Afterwards, the water discharged into the storage water tank, then started the variable frequency circulating pump to make sure the water could be flow into the closed loop, and the water flow rate and distance were simulated respectively by the monitor of flowmeter and the record of the flow time. During the re-aeration and flow, the water was sampled from the sampling point, then the COD and DO of the water were measured, and the polymer solution was prepared by the water. The viscosity of the polymer solution was determined at the simulated reservoir temperature of 45°C by rotational viscometer (BROOKFIELD, DV-II+). Finally, the feasibility of ASP flooding produced water reused to preparing the polymer solution was proved, especially the

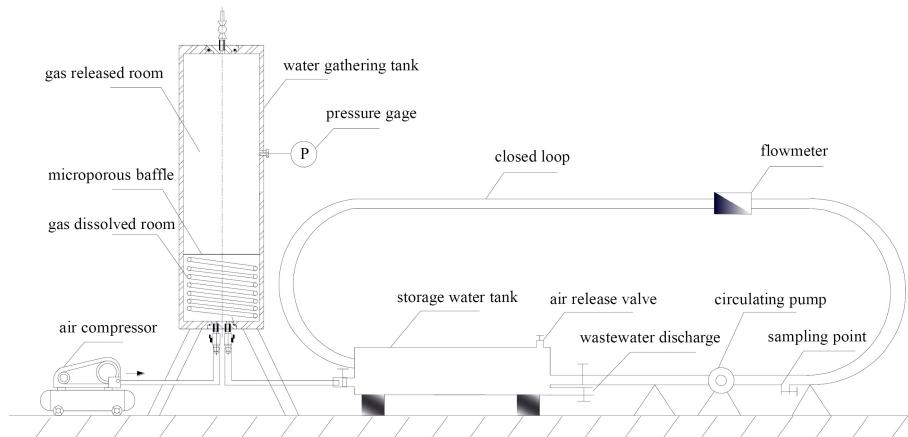
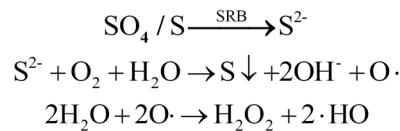


Figure 7—Schematic illustration of the re-aeration and flow simulated device

ability of controlling viscosity loss would be estimated, the DO parameters were further optimized, and the role of flow rate and distance on the produced water treatment option would also be determined.

Experimental results and discussion The iron bacteria (FB) in oilfield produced water keep the ability of oxidative degradation on hydrolyzed polyacrylamide (HP), and when the HP structure is destroyed, saprophytic bacteria (TGB) and SRB would further use the intermediate products for nutrition metabolism. Besides, the exist of SRB would contribute to the gradually reduction of sulfate radical into S^{2-} , then the oxygen free radical and hydroperoxide are generated:



The oxidative degradation of HP includes automatic oxidation process and chain cracking process²⁸. Therefore, when the oxygen free radical and hydroperoxide exist, the free radical would be generated, result in a chain automatic oxidation reaction. Furthermore, with the temperature rise and reducing substances presence, the reaction would be significantly accelerated, and the generation of polymer chain free radical (PO· and P·) would be promoted. Afterwards, the carbon chain cracking reaction is initiated due to the free radical, the cracking reaction will cause the fracture of the main chain of the polymer molecules, leading to the rapidly reduction of polymer relative molecular mass. Simultaneously, with the decarboxamidation (AM) or decarboxylic reaction, different degradation products would be generated, inducing the decrease of polymer solution viscosity. The chain oxidation reaction equation can be expressed as:

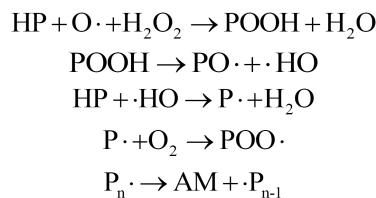


Fig.8 indicates that the DO concentration of the produced water is increased and the COD is decreased remarkably by re-aeration. When the DO concentration reaches 9.5mg/L, the decreasing amplitude of COD value is more than 70%, the viscosity of polymer solution prepared by the water with different concentrations are obviously enhanced, and the higher the concentration prepared, the better the viscosity improved, then the control ability on viscosity loss is validated. This is because the re-aeration oxidation can contribute to not only the efficient removal of reducing substances, but also the bacteria passivation

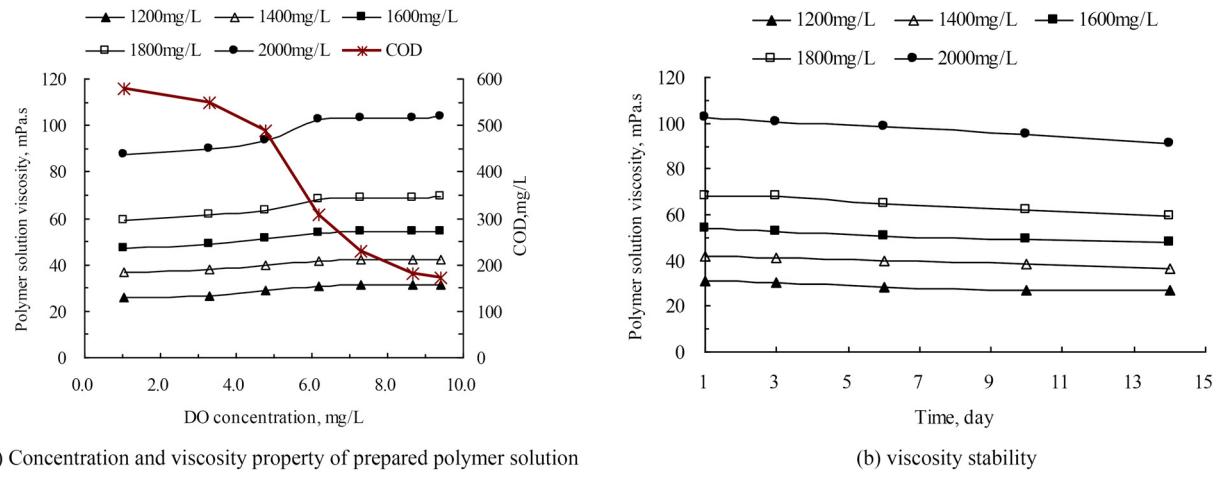


Figure 8—Relation of ASP flooding produced water DO concentration, COD and polymer viscosity

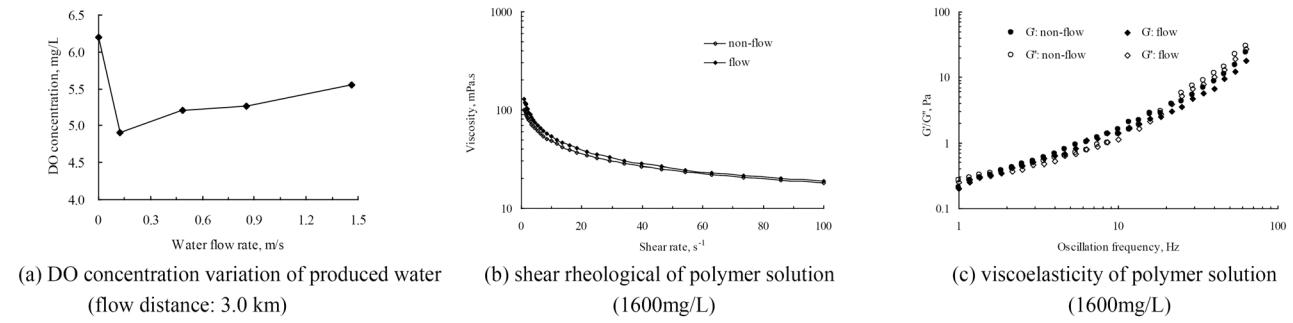


Figure 9—Influence of water flow rate on water quality and prepared polymer solution property after re-aeration

of the produced water. Consequently, the attack of chemical degradation and biodegradation on polymer molecular chain, or the destruction on its structure would be restrained. Furthermore, the concentration and viscosity property of the prepared polymer solution reveal that as the DO concentration in the water reaches 5–6 mg/L, the viscosity increasing amplitude of polymer solution with different concentrations tend to an equilibrium of 15–20%. It can be deduced that this DO content is the optimum parameter of the re-aeration. The viscosity variation behavior (Fig.8(b)) at reservoir temperature of 45°C in 15 days can also reflect that, the viscosity stability of the polymer solution system prepared by ASP flooding produced water is favorable, and the viscosity loss rate is less than 15%. The results are in agreement with the published relevant literatures about the practice of water flooding or polymer flooding produced water beneficial reuse for compounding polymer solution^{29,30}.

As Fig.9(a) and Fig.10(a) illustrate, under the comprehensive mechanism of water temperature variation and turbulence generated, there is oxygen consumption in the flow of ASP flooding produced water after re-aeration. When the flow rate is lower, the distance is longer, the oxygen consumption is obvious. And, when the flow rate is larger, the distance is shorter, the oxygen consumption is relatively fewer. However, large scale simulated experiments show that, there is no obviously variation on the prepared polymer solution properties before and after the water flow. Take the polymer solution with concentrations of 1600 mg/L and 2000 mg/L as examples (Fig.9(b), (c) and Fig.10(b), (c)), the shear resistance of the prepared polymer solution with same concentration before and after the water flow are similar, and the storage modulus (G') and loss modulus (G'') in different oscillation frequencies reflect the viscoelasticity of the two system are analogical, the rheological curves are almost coincident. This indicate after the sufficient re-aeration on the ASP flooding produced water disposed by the combined process, the feasibility of the reuse method and the control ability of the viscosity loss would not be influenced by the

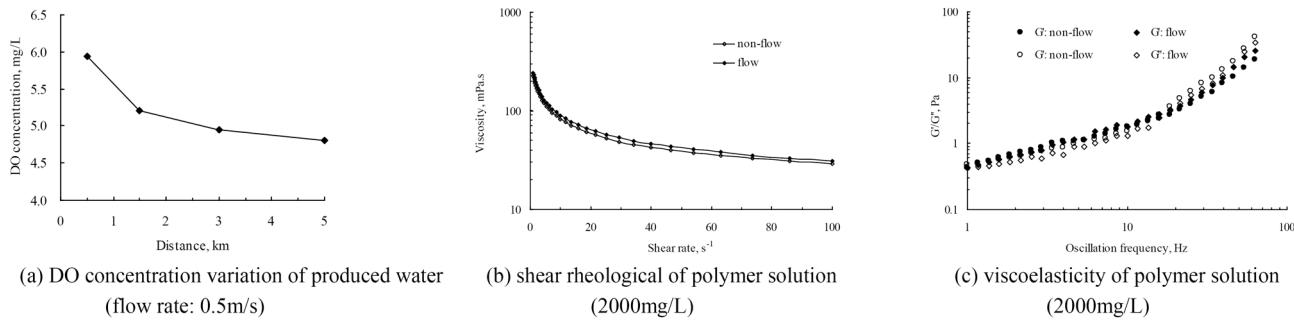


Figure 10—Influence of water flow distance on water quality and prepared polymer solution property after re-aeration

flow of preparing and injecting the polymer solution. It proves the treatment option of ASP flooding produced water is desirable.

Conclusions

1. The microcosmic emulsification behavior of ASP flooding produced water is complex, the oil-water interface electronegativity is strong and the dynamic interfacial tension decreases with the increase of interface life. The synergistic effect of these properties and the appearance of the chemicals contribute to the reduce of the interface energy, then the thermodynamic stability of the emulsion is dominated. The adsorption, insertion and coalescence between mineral particles such as quartz sand and Ca-montmorillonite and oil droplets would further deteriorate the oil-water separation efficiency.
2. The combined process is composed by sedimentation unit with aeration, lateral flow coalescence unit, dissolved air flotation unit, micro-flocculation suspended sludge blanket filtration unit and precise filtration unit. With the optimal operation conditions and parameters, the oil and suspended solid contents of the ASP flooding produced water after disposal were both lower than 20mg/L, median particle diameter was less than 5 microns and the chemical concentration was lower than 100mg/L. The disposal process operating cost was saved, power and agent expense were reduced 60.0%, the sludge amount of the ASP flooding produced water was decreased more than 70.0%.
3. Purifying effect, economical justification, and secondary pollution are the bottleneck problems and challenges adapting to the ASP flooding produced water disposal techniques. The PWRI in-situ after disposal in high permeability reservoir water flooding development, or preparing polymer solution in-situ during polymer flooding and ASP flooding are the preferable methods of recycle and reuse with zero discharge. There is no irreversible physical plugging and pollution in the re-injection of reservoir, the rheological and viscoelasticity of the polymer solution prepared with the produced water disposed by the re-aeration can be desirable achieved, and the viscosity loss control ability is not influenced by the flow rate and distance. This treatment option is worth pursuing in the industrial application of the ASP flooding EOR technology.

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