Purifying agents for produced fluid from chemical flooding in conventional and heavy oil reservoirs

G L Liu¹, F S Zhang¹, J H Sun², X N Li¹, Y Z Qu³, Z Y Zhu¹ and H M Su¹

¹Oilfield Chemistry Key Laboratory, CNPC (RIPED, PetroChina), Beijing, China
²China University of Geosciences (Beijing), Beijing, China
³CNPC Drilling Research Institute, Beijing, China
⁴E-mail: liuguoliangl@petrochina.com.cn

Abstract. Compared with water flooding, the produced wastewater quality of polymer flooding and ASP flooding has changed significantly. The effect of chemical flooding agent on the stability and purification process of oil droplets and suspended solids in wastewater was analyzed. The two-stage sedimentation-pressure filtration process and the continuous batch sedimentation-two-stage filtration process used in the treatment of chemical flooding wastewater are introduced. The application of organic flocculants, inorganic flocculants, reverse demulsifiers, chemical desiliconizing agents and other purifying agents in the treatment of chemical flooding wastewater is summarized. The key research directions of wastewater treatment from chemical flooding in the future are put forward.

1. Introduction
Chemical flooding technologies represented by polymer flooding and ASP (alkali-surfactant-polymer) flooding have been widely used in Daqing oilfield and other fields, and gained remarkable results. Polymer flooding technology started large scale application in Daqing oilfield in 1996. After polymer flooding was used, annual oil production reached above 10 million tons in 2017 and the cumulative oil production has reached 192 million tons as of 2017[1, 2]. In Shengli Oilfield and Xinjiang Oilfield, pilot field tests of polymer flooding have been successively carried out and its industrial application has been promoted [3, 4]. In 2014, the annual oil production from ASP flooding reached 2.25 million tons was adopted, with the cumulative oil production 12.38 million tons in Daqing oilfield [1]. It shows that ASP flooding may increase oil recovery rate by more than 20% compared with water flooding [5]. Chemical flooding will provide important technical support for stable production and sustainable development of highwater-containing oilfields in China.

Moreover, various chemical agents such as polymers remains in the produced liquid, which was used in the injection system of chemical flooding. Consequently, it is very difficult to dehydrate produced liquid and purify the sewage. Let us take ASP flooding as an example. As polymers, alkali and surfactant remain in the produced wastewater, there are increase in sewage viscosity, serious oil emulsification and suspension particles growth [6]. Furthermore it caused difficulty in oil-water separation and suspended solid removal. At present, ineffective wastewater treatment result in the water quality of treated sewage frequently failing to meet the water-injection requirements.

This paper is to introduce characteristics of the oilfield wastewater produced from polymer and ASP flooding. Besides, the current technologies and new progress for such sewage treatment is to
summarize. The research progress of wastewater purifying agents is discussed prominently. And we put forward the key research direction for sewage treatment technology.

2. Water quality characteristics of produced wastewater from oilfield chemical flooding

Various chemicals injected in a chemical flooding process deteriorate the produced wastewater quality. As shown in Table 1, the water data of wastewater produced in several types test stations was listed, including polymer flooding, weak-alkali and strong-alkali APS flooding carried in Daqing oilfield. The wastewater aforementioned contains the polymers, above 1,000mg/L at the most. The sewage viscosity increased with the increase of polymer concentration, above 5.0mPa.s at the maximum. Compared with the produced wastewater from weak-alkali ASP flooding, the wastewater from strong-alkali ASP flooding has a higher pH value and Si content. Oppositely, the produced wastewater from weak-alkali ASP flooding has HCO$_3^-$ and CO$_3^{2-}$ ions with a higher concentration. And there is little difference in the contents of surfactants in the produced wastewater from ASP flooding, around 50mg/L.

| Project | No.360(polymer flooding)[1] | Beierxi(Weak-base ASP flooding) [7, 8] | Xing’.erzhong(Strong-base ASP flooding)[9, 10] | No.291(ASP flooding)[11, 12] |
|---------|----------------------------|---------------------------------|---------------------------------|----------------------------|
| pH value | 7.96                      | 8.2-8.6                         | 9.1                             | 9.4-10.4                   |
| Viscosity (mPa.s) | 0.795                   | 3.0(40℃, 10s$^{-1}$)          | 1.9(40℃，7.43s$^{-1}$)           | 5.1                        |
| Polymer (mg/L)      | 568.0                    | 1168                            | 93.4                            | 635-740                    |
| Surfactant (mg/L)   | 53                       | 58                              | 20.4                            | 56                         |
| Mg$^{2+}$(mg/L)     | 6.0                      | 5.4                             | 5.2                             | 10.0                       |
| Ca$^{2+}$ (mg/L)    | 30.0                     | 40.8                            | 18.2                            | 10.8                       |
| Si(mg/L)            | -                        | 30.4                            | 388.8                           | 103.0                      |
| HCO$_3^-$ (mg/L)    | 1548.8                   | 135                             | 2563                            | -                          |
| CO$_3^{2-}$ (mg/L)  | 39.0                     | 4404                            | 675                             | -                          |

Chemical oil-displacing agents have serious effect on purification of sewage by changing physical and chemical states of oil droplets and particulate matters in produced wastewater. This is manifested in: (1) Part of polymer hydrolyzed polyacrylamide (HPAM) or xanthan gum is capable of increasing the viscosity of sewage, reducing the separation rate of oil and particulate matters in water, worsening flocculant effect, and facilitating the formation of O/W emulsion [6]; (2) Heavy alkyl-benzene sulphonate or petroleum sulphonate surfactant is capable of lowering oil-water interfacial tension, water and Zeta potential, increasing the degree of emulsification, enabling particle size of oil droplets to become smaller, and reducing the mid-value of partical size to about 10 μm [7, 13]; (3) Alkali components such as NaOH, Na$_2$CO$_3$ or Na$_2$SiO$_3$ may dissolve out Si and Al from stratum mineral, and convert them into scale, colloidal particles, secondary mineral, and other insoluble particles, increasing the quantity of suspended solids.

Table 1.Water quality data of produced water from polymer and ASP flooding in Daqing oilfield.

The stability of oil droplets and solid particles in ASP flooding sewage was more complicated [14-16]. Kang Wanli et al. [17] studied simulated wastewater(NaOH/ petroleum sulphonate /HPAM). They found surfactants and alkali can reduce oil droplets size; polymers can significantly increase water-phase viscosity; both effects prevent oil droplets from getting larger and coalesced. According to liu Yang et al. [6], the adsorption of surfactants (alkyl/benzene sulphonate) and polymers on oil droplets results in: (1) The surface of oil droplets turns from hydrophobic to hydrophilic, and it's difficult to approach oil droplets; (2) Negative charge density increases on oil dropletssurface, Zeta potential decreases significantly, and the repulsion force of oil droplets increases; (3) There's an increase in oil droplet surface elasticity and the difficulty in coalescence.
3. Current treatment process for produced wastewater from oilfield chemical flooding

The wastewater treatment process of polymer flooding and ASP flooding was developed based on water flooding process. Taking Daqing oilfield as an example, the sewage treatment process in water flooding was mainly two-stage sedimentation (gravity sedimentation-coagulation sedimentation) and pressure filtration three-stage treatment process [13]. A small number of process used coagulation sedimentation-air flotation-pressure filtration, transverse flow coagulation deoiler-pressure filtration, air flotation-pressure filtration process. Two-stage sedimentation and two-stage pressure filtration were also used in the treatment of polymer-containing wastewater (for example, the North 13 Sewage Treatment Station in Sabei Oilfield). Settlement time was 4h and 2h respectively. A small number of treatment stations adopted two-stage sedimentation and one-stage filtration process. Settlement time was 10 h and 5 h [18, 19], respectively. Since 2005, Daqing Oilfield has built ASP sewage treatment stations [20]. The main process adopted was aeration sedimentation-high efficiency oil-water separation-double filter media filtration [21]. In recent years, the new process of sequential batch sedimentation (Figure 1) has been emphasized and developed.

The new sequential sedimentation-filtration process significantly improves the treatment effect of wastewater from chemical flooding. It can achieve continuous settlement and sequencing batch sedimentation of wastewater. No or little water purifying agents can be added for a low content of oil-displacing agent, yet effective water purifying agents should be added for a high content of oil-displacing agent to meet the requirements for oilfield injection (both suspended solids and oil content are less than 20mg/L). On the other hand, if chemical flooding injection solution is prepared with purified water, a deep treatment process is also needed to remove salt and polymers from wastewater [22, 23].

![Figure 1. Process of sequencing batch sedimentation used in oilfield wastewater treatment.](image)

4. State of the purifying agents for chemical flooding wastewater

For the problems about oil-water separation and suspended solids removal concerning produced wastewater from ASP flooding, Chinese researchers have made certain achievements by adopting various types of wastewater treatment processes, including reverse demulsifier, organic or inorganic or composite flocculant, chemical desilicator, water quality stabilizer, and oxidant.

4.1. Reverse demulsifiers

Wei Li et al. [24] have treated the produced wastewater (including HPAM 272.5mg/L, total alkalinity 3,580mg/L, surfactant 36.4mg/L, the pH value 9.40, viscosity 1.16mpa.s) from ASP flooding in a plant of Daqing oilfield with QP555 oil remover. Field tests showed that under the conditions of water inflow/outflow rate 50-240L/h, quantity of chemicals injection 75mg/L, mixer degree 130r/min,
stirring time 6 min and capture time 15 min, the oil content of wastewater may be reduced from 125-156 mg/L to less than 50 mg/L, meeting the requirement for water inflow of oilfield filtration equipment, with the wastewater treatment cost not more than 4.83 CNY/m³ (0.695 US$/m³).

Liu Lixin et al. [25, 26] have synthesized three types of different reverse demulsifiers of polyquaternary ammonium salt by using epichlorohydrin and dimethylamine as monomers as well as ethylenediamine, n-butylamine and polyethylene polyamine as crosslinkers. For simulated wastewater from weak-alkali ASP flooding, when reverse demulsiifier was added to 80 mg/L, the oil removal rate may reach 94% and light transmittance up to 11%. The results show that reverse demulsifier was superior to CW-01 and SP169 polyehter-type demulsifiers. The reverse demulsifier may be a good match to the flocculant polymeric aluminum ferric sulphate (PAFS). When the PAFS was added to 800 mg/L, the oil removal rate will be 97% and the light transmittance 77%.

4.2. Organic floculants

The performance of commonly used floculants such as polyaluminum chloride (PAC) and cationic polyacrylamide (CPAM) in oilfields is seriously affected by the large amount of HPAM, surfactant and alkali contained in the ASP flooding wastewater [27]. The presence of anion HPAM in water not only increases the quantity of flocculant required, but also decreases the effect of floculant. The anion HPAM in water may make electrical neutralization reaction with floculant to form viscous floculant, which is not conducive to subsequent filtration treatment.

Lu Jiao et al. [28] have synthesized cationic starch modified floculant by introducing cationic monomer diallyl dimethylammonium chloride (DADMAC) on the basis of starch grafted acrylamide. Properties of the floculant were affected by cationic charge and relative molecular mass. When Al₄(SO₄)₃ was mixed into the wastewater from ASP flooding in Daqing oilfield, the floculant prepared at m(DADMAC):m(soluble starch)=1:9, was capable of removing oil effectively, suspended substance and polymer from the wastewater. When flocculant was added to be 50 mg/L, the light transmittance of treated wastewater will reach 95%.

Liu Lixin et al. [29] have modified hyperbranched polyamines (PAMAM) into end-group positive ions by using cationic monomers. The modified products featured high reactivity and flocculation advantages of cationic polymers. Cationic monomers include methacryloxyethyl trimethylammonium chloride (DMC), acryloyloxyethyl trimethylammonium chloride (DAC), and methacryloxyethyl dimethylammonium bromide (DMB). With regard to simulated wastewater from ASP flooding, prepared PAMAM-DMC had the best flocculation performance under the conditions — reaction temperature 60 °C, reaction time 36 h, and m (DMC):m (PAMAM) = 1.2:1.

4.3. Inorganic floculants

Wang Yu et al. [30] have prepared polymeric aluminum silicate floculant PSiAS-1 with Na₂SiO₃·9H₂O, sulfuric acid, and Al₄(SO₄)₃·18H₂O. Treating produced wastewater from polymer flooding with 50 mg/L PFS (polyferric coagulant), 200 mg/L PSiAS-1 and 8 mg/L settling agent can reduce turbidity and remove calcium, magnesium, oil content, and suspended solids. In addition, the content of residual polymers in wastewater was also remarkably reduced, with no reduced ferric ions and sulfide contained.

Shen Yuxing et al. [31] have used inorganic coagulant + organic floculant to treat the produced wastewater (including HPAM 112 mg/L, pH value 9.2) from ASP flooding in Daqing oilfield. Of the coagulants, CaCl₂ and ZnCl₂ had poor effects, FeCl₃ and polymeric aluminium(iron) were relatively better, and composite aluminium salt DA-1 has the best effect. Mixing 40 mg/L DA-1 and 10 mg/L of organic floculant DP-103 with the produced water at the temperature below 40 °C may make light transmittance of wastewater rise from 61.5% to 99.4%.

Targeted at wastewater from strong-alkali ASP flooding in Xing’erzhong test station of Daqing oilfield, Zhao Fengling et al. [32] have developed a composite water-cleaning agent CF1002 consisting of pH regulator, coagulant and coagulant aid. The wastewater contained 303 mg/L HPAM, 77.5 mg/L oil, and 88 mg/L suspended solids and whose pH value was 9.53. After composite water-cleaning agent
of 3,030mg/L was added into the incoming water, the oil content of inflow water to the primary filter dropped to 2.3mg/L, and the content of suspended solids in outflow water dropped to 6.29mg/L. The yielding wastewater meets the control index of high-permeability oil deposit re-injection by produced water, with the treatment cost 12.4 CNY/m$^3$ (1.78 US$/m^3$).

4.4. Other water purifying agents

As dissolution reaction between alkali and formation during ASP flooding in conventional oil reservoirs, the silicon content in the produced liquid will increase. In the thermal recovery of heavy oil reservoirs, there is also a high concentration of silicon in the produced liquid. Therefore, chemical silica removal agents were often used.

Zhao Zhenxing et al. [33, 34] have invented the integrated treatment process of air flotation silicon removal and suspended matter reduction which was aimed at produced wastewater from ASP flooding. The process has been successfully applied in a test station in Daqing oilfield. After demulsification, the ASP flooding wastewater entered the regulating tank for natural sedimentation. The wastewater pH after sedimentation was adjusted to 10-13 with agents (including pH regulator and silicon remover) [35], then sent to the air float tank. Much micro bubbles were attached to the suspended material to make it all float on the water surface. Finally, the air-flotation outflow water was sent to the fiber ball filter and the fiber bundle filter for filtration, and the SS content of the filtered water was less than 20mg/L.

Cheng Jiecheng et al. [36-38] mixed complexing agents and alkaline agents into the ASP flooding sewage in an effort to prevent divalent metal ions, polyvalent metal ions, silicate, silicate ions, and partial acid radical ion from being supersaturated in water phase, thus inhibiting carbonate, sulfate, hydroxide, silicate, silicon aluminate and amorphous silica particles from generating. In such a way, we may radically tackle the problem that inorganic particles have bad effect on produced liquid from ASP flooding in oil-water separation and produced water treatment. The complexing agents used were composed of ethylenediamine tetaacetae disodium salt and ethylenediamine tetramethylphosphonic acid; the alkali agents used include sodium hydroxide and sodium carbonate.

5. Conclusions and suggestions

Above all, new progresses and various purifying agents were developed to treat wastewater produced from chemical flooding. But the purification effect was not very satisfactory due to the complexity of chemical flooding sewage. The following work should be conducted for treatment of produced wastewater from polymer and ASP flooding:

(1) Strengthen the monitoring of the water quality of produced wastewater from polymer flooding and ASP flooding, including the important parameters affecting the water quality, such as polymer content, viscosity, alkali and silico-aluminum ions, so as to provide support for the research on targeted wastewater treatment process and treatment agent. Improve and establish the methods for determining content of the suspended solids, silicon content, and other water-quality parameters in wastewater from chemical flooding. Make research on the formation process, stability mechanism and influencing factors of colloids and suspended solids in the water aforementioned.

(2) Make further research and development of polysilicate metal salt flocculant, chemical silicon remover, anionic, non-ionic and weak cationic organic flocculant and other wastewater treatment agents, so as to solve a series of problems caused by anionic-polyacrylamide polymers in wastewater.

(3) Further optimize the existing process and conduct in-depth research on new process equipment, including the advanced catalytic oxidation method, magnetic separation method, and electrochemical method, in order to improve quality of wastewater and the removal effect of crude oil, colloidal particles, and other impurities in wastewater.

References

[1] Xia F J, Guo S J, Xu D H, et al. 2017 Env. Protec. and Gas Fields 27 pp 34-37
[2] Zh W, Xu W J, Lu W N, et al. 2000 Petro. Plan. & Eng.3 pp 13-15
[3] J Z J, L J X, W L X. 2008 Oil-Gas field Surf. Eng. 3 pp 41-43
[4] Wang Y, Lin L L, Si S X, et al. 2018 Oilfield Chem. 35 pp 356-361
[5] Wang D, Li J X, Wei L X. 2008 Oil-Gas field Surf. Eng. 3 pp 44-46
[6] Liu Y, Li J X, Wang D. 2008 Foreign Oilfield Eng. 11 pp 5-8
[7] Wu D, Wang C, Zhao F L, et al. 2015 Fine and Spec. Chem. 23 pp 27-33
[8] Liu W J 2013 Fine and Spec. Chem. 21 pp 16-19
[9] Wu D, Meng X C, Zhao F L, et al. 2004 Fine Chem. 1 pp 23-25
[10] Wu D, Yu G, Meng X C. 2003 Indus. Wat. Treatment1 pp 20-22
[11] Guo Q N. 2016 Chem. Eng.&Equip. 04 pp 254-258
[12] Wang H Y. 2018 Chem. Enter. Manag. 18 pp 152-153
[13] Chen Z X. Shu Z M. 2014 Indus. Water & Wastewater 1 pp 36-39
[14] Deng S B, et al. 2009 Collo. and Surf. 332 pp 63-69
[15] Li J X, Jiang N, Wu D, et al. 2008 Oilfield Chem. 3 pp 293-296
[16] Fang Y. 2009 China Water and Wastewater 10 pp 79-82
[17] Kang W L, Shan X H, Li Y, et al. 2011 Chem. Eng. of Oil and Gas 6 pp 628-631
[18] Zhang L Z. 2017 Chem. Eng.&Equip. 2 pp 100-101
[19] Zhao L C and Li J X. 2000 Gas field Surf. Eng. 4 pp 9-11
[20] Li Y, Cheng J F, Cheng J S. 2010 Oil-Gas field Surf. Eng. 11 pp 41-42
[21] Wu Y X. 2015 Inn. Mong. Petro.Industry 21 pp 121-123
[22] Karapinar N. 2003 Inter. Journal of Mineral Proc. 1 pp 45-54
[23] Pan G Q. 2018 Chem. Enter. Manag. 15 pp 13-14
[24] Wei L, Xia F J, Xu D H, et al. 2010 J of Harbin Univ. of Comm. 5 pp 545-547.
[25] Liu L X. Hao S S, Wang X C, et al. 2010 Ind. Wat. & Was. 5 pp 70-73
[26] Jiang H M, et al. 2008 Chi. Rur. Wat. and Hydro. 8 pp 40-43
[27] Ma J, Zhao X F, Zhu W, et al. 2010 Ind. Wat. & Was. 3 pp 62-65
[28] Lu J, Peng B, Li M Y. 2009 J of Chi. Univ. of Petro. 1 pp 127-130
[29] Liu L X, Cui L Y, Zhao X F, et al. 2011 Sci. & Tech. In Chem. Indu. 1 pp 1-4
[30] Wang Y, Lin L L, Si S X, et al. 2018 Oilfield Chem. 2 pp 356-361
[31] Shen Y X, Fu S B, Xu D H, et al. 2006 Journal of Petro. and Nat. Gas 6 pp 169-171
[32] Zhao F L, Wu D, Cai X, et al. 2010 Fine and Spec. Chem. 7 pp 45-47
[33] Ma Z J,Wang L H,Yi XL. 2009 Fine and Spec. Chem. 13 pp 21-22
[34] Zhao Z X, et al. 2008 CN 101264990
[35] Gao Q H, Qian H J, Hou Z F. 2010 Oil-Gas field Surf. Eng. 4 pp 16-17
[36] Du D., Wu D., Hou Z F. 2010 Oil-Gas field Surf. Eng. 4 pp 16-17
[37] Cheng J C, et al. 2007 CN 101020815
[38] Wu D, et al. 2008 CN 101235282