

Research on Ternary Composite Flooding Produced Water Treatment Process

Jinglong Bai, Litao Luo

North China University of Science and Technology, Tangshan 063210, China

Abstract

This paper introduces the ternary composite drive technology and the characteristics of the technology. The characteristics of ternary composite flooding produced water were sorted out, and the characteristics of complex organic composition, poor biochemical treatment, high oil content, high suspended solids content, high viscosity and high emulsification degree were sorted out. Three ternary composite flooding produced water treatment processes were introduced. Under the condition of ensuring that the effluent meets the requirements of reinjection water, the advantages and disadvantages of the three processes are compared, and finally the third process flow is determined to be the optimal option. The process can not only effectively improve the treatment effect of ternary composite flooding produced water, but also overcome the shortcomings in the conventional process, improve the feasibility of the process and reduce the cost.

Keywords

Ternary Composite Flooding; Produced Water; Electrochemistry.

1. Introduction

The ternary composite flooding technology is to add alkali, surfactants and polymers to the injected water to form a ternary composite system, which displaces the crude oil that cannot be recovered by conventional water flooding and polyflooding, so as to greatly improve the recovery rate of crude oil^[1]. Compared with the traditional oil recovery technology, the ternary composite flooding oil recovery technology can significantly improve the oil displacement efficiency, make up for the shortcomings of the traditional process, reduce the production cost of the oil production process, and greatly improve the efficiency of the oil recovery process and the utilization rate of crude oil^[2].

However, the water quality of ternary composite flooding produced water is very complex, containing a large amount of oil displacement agents in addition to suspended solids, oils, dissolved salts, dissolved gases, microorganisms and organic compounds. Due to the synergistic effect of the ternary composite system, the ternary produced water system produces serious emulsification, smaller particle size of oil droplets, accelerated proliferation of microorganisms, and increased viscosity of produced water, which in turn leads to the increase of the content of suspended particulate matter in the produced water, and the increase of the sinking and floating resistance of oil droplets and suspended solids in the water^[3]. Therefore, the process of researching and treating ternary composite flooded produced water has to be accelerated.

2. Characteristics of Ternary Composite Flooding Produced Water

The composition of produced water in oilfields is complex, and the composition of produced water varies greatly in different sections. Produced water is produced under high temperature and high pressure conditions, and contains a large number of complex heterogeneous components such as salts, crude oil, suspended solids, harmful gases and organic matter. During the dehydration process, demulsifiers and bleaching agents are also added. Due to the different

oil recovery methods, the composition of oil layer water in reservoirs in different regions is different, and the produced water generally has the characteristics of high content of petroleum substances, high degree of mineralization, high content of refractory organic matter, high content of suspended solids, small particles, a large number of microorganisms and a large number of scalable ions^[4]. In addition to the above commonalities, ternary composite flooding produced water also has its particularities. The ternary composite oil displacement system contains a large amount of alkali, surfactant and polyacrylamide, in which the alkali can interact with the substances in the crude oil to form a surfactant. These surfactants are adsorbed with surfactants at the oil-water interface and solid-phase particles. Surfactants can also reduce the interfacial tension between oil and water, and a large number of polymers increase the viscosity of produced water^[5]. The main characteristics of ternary composite flooding produced water can be summarized as follows.

2.1. The Organic Composition is Complex and the Biochemical Processing is Poor.

There are many types of organic matter in oilfield wastewater, including hydrocarbons, a variety of surfactants and various stabilizers^[6]. Sewage often contains organic substances such as benzene, phenols, polycyclic aromatic hydrocarbons, organic acids, nitrides, ketones, esters, aliphatic hydrocarbons, and aldehydes^[7].

2.2. The Viscosity is Large and Often Contains Polymers.

The viscosity of oilfield wastewater increases with the polymer concentration, which increases the difficulty of subsequent flocculation, sedimentation and solid-liquid separation. Water-soluble polymers, such as acrylamide polymers and guar gum, can clog formation pores and cause serious damage to the formation^[8].

2.3. High Oil Content and High Degree of Emulsification.

The particle size of the oil droplets is about 30 μ m. It is easy to adsorb charged particles, is negatively charged, has strong stability and is not easy to separate. As a common pollutant, emulsified crude oil will pollute the natural environment due to illegal discharge, and the emulsified oil entering the formation will often reduce the formation permeability and reduce the oil recovery^[9-12].

2.4. High Content of Suspended Solids, Including Sediments, Clays, Corrosion Products and Other Suspended Solids Generated in the Production Process.

Suspended solids in oilfield wastewater can become the carrier of organic treatment agents and oil droplets, hindering their destabilization and separation^[13]. The accumulation of a large amount of solid waste will cause a waste of space, and will also produce dust or leachate into the environment under the action of wind, sunlight and rainwater, causing serious secondary pollution^[14].

3. Three-way Composite Flooding Produced Water Treatment Process

3.1. Air Float Sedimentation + Biochemical Oxidation + Advanced Oxidation + Secondary Filtration

Song Xuefeng and others^[15] The treatment process of air float sedimentation + biochemical oxidation + advanced oxidation + secondary filtration was proposed.

The ternary composite flooding produced water first enters the air flotation settlement unit, and most of the oil content and suspended solids in the water are removed, and then enters the biochemical oxidation unit, at this stage, the stability of the produced water is destroyed to a

certain extent, and the SS and COD_{cr} are further removed and oil content, and then enter the advanced catalytic oxidation unit, using the combined oxidation of ozone and ultraviolet rays, the polymer is broken to a certain extent, reducing its stability, and finally entering the two-stage sand filter unit to adsorb and intercept SS and mucous particles in the produced water, so as to reduce the turbidity of the water and reach the standard as scheduled.

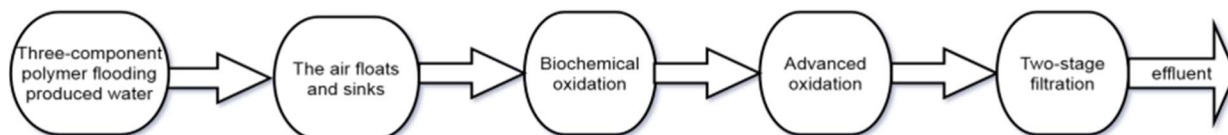


Fig.1 Process flow diagram of scheme 1

In the process of ternary composite flooding produced water treatment, the air flotation process is still the preferred treatment method, among which the partial reflux dissolved air flotation method has attracted much attention because of its advantages such as high foam capacity, small bubble size, and good solid-liquid separation effect. Based on the principle of similar miscibility, the suspended solids or oil droplets of the hydrophobic group in the wastewater to be treated can be well adsorbed on the tiny bubbles, and after the particles are adsorbed on the bubbles, they form a floc with a smaller density than water, which floats to the water surface to form a scum layer that can be scraped off by a slag scraper.

It is a useful exploration to use biochemical technology to routinely treat ternary composite flooded produced water. In this study, the sediment of the ternary composite flooding sedimentation tank was taken as the research object, and the indigenous flora with special salt resistance and harmful substance resistance was screened out, and after domestication, culture and proliferation, it was compounded into a composite bacterial line SW1 bacterial agent, which was applied to the water body. The results show that the biodegradability of produced water is improved by the anaerobic section, and the acidification pH value fluctuation and the self-metabolism of anaerobic and aerobic bacteria and aeration shear have different effects on the indexes of oil, COD_{cr} , viscosity and polymer, and the deoiling and destabilization are initially achieved. To a certain extent, the biological method broke the stable state of the produced aqueous solution, which provided favorable conditions for the further removal of SS.

Advanced Catalytic Oxidation Unit Process Catalytic Mode: Ultraviolet Irradiation, Ozone Generation Mode: Air Source, Ozone Dosing Mode: Contact Oxidation Tower. If the strong oxidation of reactive oxygen species and hydroxyl radicals generated by ozone is used, some organic substances can be directly oxidized into inorganic substances, and the polymer can be broken to a certain extent, thereby reducing the stability of produced water, which is conducive to the separation and filtration of SS.

The primary filter material of the sand filter unit is 0.5~0.8mm quartz sand, and the secondary filter material is 0.3~0.5mm quartz sand. Compared with the commonly used filter materials such as glauconite and magnetite, the filter material with smaller particle size is used to adsorb and intercept the suspended particulate matter and viscous particles in the produced water to achieve the purpose of reducing the turbidity of the water. This is mainly due to the biochemical and oxidation processes of pretreatment that change the structure of the produced water, so that the adhesion of the solution is reduced, the SS is easier to fall off, the filtration and backwashing effect is better, and the filter media is not hardened.

The section headings are in boldface capital and lowercase letters. Second level headings are typed as part of the succeeding paragraph (like the subsection heading of this paragraph). All manuscripts must be in English, also the table and figure texts, otherwise we cannot publish

your paper. Please keep a second copy of your manuscript in your office. When receiving the paper, we assume that the corresponding authors grant us the copyright to use the paper for the book or journal in question. When receiving the paper, we assume that the corresponding authors grant us the copyright to use the paper for the book or journal in question. When receiving the paper, we assume that the corresponding authors grant us the copyright to use.

3.2. Natural Sedimentation Tank + High-speed Disc Centrifugal Separator + Buffer Tank before Filtration + First-class Glauconite Magnetite Double-layer Filter Tank + Export and Backwashing Water Tank

Xia Fujun^[16] The high-speed centrifugal method was proposed to treat the ternary composite flooding produced water.

The ternary composite flooding produced water first removes the floating oil and dispersed oil through the natural sedimentation tank, and then further removes the emulsified oil and suspended solids in the produced water through the high-speed disc centrifugal separator, and the effluent after the oil-water separation of the high-speed disc centrifuge flows into the buffer tank before filtration, and then enters the first-class glauconite magnetite double-layer filter material filter after the filtration lifting pump is pressurized, and the filtered water reaches the standard, and then passes through the external transmission and backwashing water tank, and is pressurized and transported to the water injection station for reinjection. After filtration, the final effluent quality meets the requirements of the oilfield water quality index of poly-reinjection water, oil concentration and suspended solids concentration of $\leq 20\text{mg/L}$.

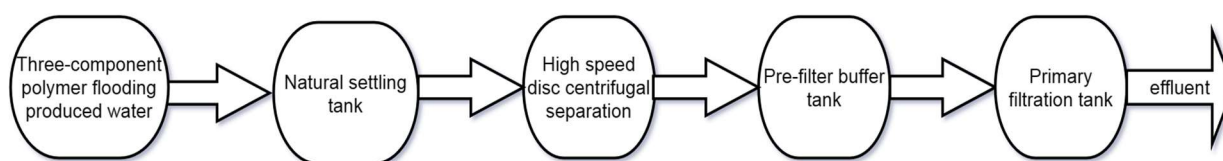


Fig.2 Process flow diagram of scheme 2

Principle of high-speed disc centrifugal separation technology: At present, high-speed disc centrifuge is mainly used in mineral oil, dairy products, starch and pharmaceutical industries, but has not been developed and applied in China's oil and gas produced water treatment. The principle of centrifugal separation is a vertical centrifuge, the drum is installed on the upper part of the vertical shaft, and it rotates at high speed by the transmission device driven by an electric motor. The suspension (or emulsion) is fed into the bowl by a feed pipe located in the center of the bowl. As the suspension (or emulsion) flows through the gap between the discs, the solid particles (or droplets) settle onto the discs by the centrifuge to form a sediment (or liquid layer). The sediment slides along the surface of the disc and detaches away from the disc and accumulates in the part with the largest diameter in the bowl, and the separated liquid is discharged from the drum from the outlet respectively, and the solids accumulated in the drum are discharged from the drum without stopping the machine through the slag discharge mechanism. The sedimentation separation is a spin of the inclined baffle vessel 90° and around the shaft to form a centrifugal body that continuously separates the solid particles^[16].

The glauconite filter material selected in this process is compared with quartz sand, Mechanical strength (Wear rate + breakage rate) and the filtration effect are significantly improved, After regeneration, the residual oil content on the surface of the filter media is lower than that of quartz sand, and the filter material is combined with the magnetite filter material to form a double filter tank, This dual media filter is a primary filtration application^[17].

3.3. High-efficiency Air Flotation Tank + Electrochemical Device + Ultrafiltration

Ao Lu and others^[18] The combined treatment of ternary composite produced water by electrochemical and ultrafiltration was proposed.

The produced water first enters the high-efficiency air flotation tank to remove most of the suspended particles, oil content and other pollutants in the water; then through electrochemical treatment, most of the PAM is completely oxidized, broken and degraded, so as to improve the water quality characteristics and realize the effective removal of oil-water separation and SS; secondly, through ultrafiltration treatment, the small molecule oil and SS are further removed in depth to ensure that the effluent is stable and up to standard, and the water can directly enter the clear water pool after reaching the standard, and finally re-inject into the low-permeability oil layer or reuse it for ultrafiltration backwashing.

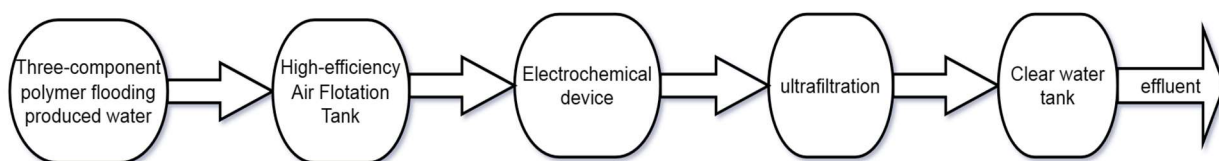


Fig.3 Process flow diagram of scheme 3

Electrochemical devices. In view of the high degree of emulsification of the ternary composite flooding produced water, the water quality characteristics are changed through electrocatalytic oxidation, which is convenient for the removal of polymers and suspended solids, and ensures that the effluent meets the inlet water requirements of subsequent ultrafiltration^[19]. The ternary produced water has complex composition, high emulsification degree and high viscosity, and the multi-functional and high-efficiency characteristics of electrocatalytic oxidation technology in its treatment are more prominent^[20].

Ultrafiltration. Ceramic membrane filter is used^[21], deeply intercept the oil and solid suspended solids carried in the effluent of the electrochemical device, so that the effluent water quality finally meets the standard.

4. Process Comparison

Table 1. Advantages and Disadvantages of Process Flow

| Process | merit | shortcoming |
|--|--|--|
| Air float sedimentation + biochemical oxidation + advanced oxidation + secondary filtration | It reduces the difficulty of filter flushing, improves the stability of process operation, and continuously meets the requirements of reinjection. | It occupies a large area, has high energy consumption and high operating costs |
| Natural sedimentation tank + high-speed disc centrifugal separator + buffer tank before filtration + first-class glauconite magnetite double-layer filter material filter tank + export and backwashing water tank | Reduced footprint by shortening the residence time of the oil-water separation of sewage saves investment and subsequent operating costs. | The treatment effect is worse than the other two processes, and the operation is more complicated |
| High-efficiency air flotation tank + electrochemical device + ultrafiltration + clear water tank | Its structure is less, so the process occupies a small area, the investment is less, the process operation is more stable, and the effluent quality meets the water quality standard of reinjection water. | A range of chemicals need to be added to the treatment, and electrocatalytic oxidation is required |

5. Conclusion

1) Ternary composite flooding is a new way to greatly improve oil recovery, which replaces the crude oil that cannot be recovered by conventional water flooding and polyflooding by adding alkali, surfactants and polymers to the injected water to form a ternary composite system. Ternary composite flooding produced water has ①The organic components are complex, and the biochemical treatment is poor;②High oil content, presence of dissolved oil and emulsified oil;③High content of suspended solids, including sediments, clays, corrosion products and other suspended solids generated in the production process;④The viscosity is large, often containing polymers;⑤High degree of emulsification.

2) Compare the three process flows, process flow 1: air float sedimentation + biochemical oxidation + advanced oxidation + secondary filtration, process flow 2: natural sedimentation tank + high-speed disc centrifugal separator + buffer tank before filtration + first-stage glauconite magnetite double-layer filter material filter tank + export and backwash water tank Process flow 3: high-efficiency air flotation tank + electrochemical device + ultrafiltration + clear water tank. Based on the consideration of effluent quality, construction area, construction and operation costs, etc., the process flow 3: high-efficiency air flotation tank + electrochemical device + ultrafiltration + clear water tank is the best option. It is expected that the third combination process can be more used in the reuse of ternary composite flooding oilfield wastewater in the future.

References

- [1] Chemical Engineering and Equipment,2023,(10):178-179+181.
- [2] Application of ternary composite flooding oil recovery technology in petroleum exploitation[J]. Chemical Engineering and Equipment,2021,(08):95+94.
- [3] Huang Bin,Wang Chen,Fu Cheng,Fu Siqiang,Huang Likai,Zhang Weisen.Research progress on ternary composite flooding produced water treatment[J].Chemical Industry and Engineering Progress,2020,39(10):4238-4247.
- [4] Li Zhe, Zhang Lu, Liang Shujuan, et al.Research progress of produced water treatment technology in oilfield[J].Chemical Engineer,2024,38(03):59-62+103.
- [5] Ma Zekun.Study on stability mechanism of ternary composite flooding produced water[D].China University of Mining and Technology,2019.
- [6] Chen L, Bai B. Equilibrium, kinetic, thermodynamic, and in situ regeneration studies about methylene blue adsorption by the raspberry-like TiO₂@yeast microspheres[J]. Industrial & Engineering Chemistry Research, 2013, 52(44):15568-15577.
- [7] Al-Ghouthi M A, Al-Kaabi M A, Ashfaq M Y, et al. Produced water characteristics, treatment and reuse: A review[J]. Journal of water Process Engineering, 2019, 28:222-239.
- [8] Pu W F, Liu R, Wang K Y, et al. Water-soluble core-shell hyperbranched polymers for enhanced oil recovery[J]. Industrial & Engineering Chemistry Research, 2015, 54(3):798-807.
- [9] Tong K, Zhang Y, Liu G, et al. Treatment of heavy oil wastewater by a conventional activated sludge process coupled with an immobilized biological filter[J]. International Biodeterioration & Biodegradation, 2013, 84:65-71.
- [10] Berdugo-Clavijo C, Sen A, Seyyedi M, et al. High temperature utilization of PAM and HPAM by microbial communities enriched from oilfield produced water and activated sludge[J]. Amb Express, 2019, 9(1):1-10.
- [11] Yan M, Zhao L, Bao M, et al. Hydrolyzed polyacrylamide biodegradation and mechanism in sequencing batch biofilm reactor[J]. Bioresource technology, 2016, 207:315-321.

- [12] Zhao L, Bao M, Yan M, et al. Kinetics and thermodynamics of biodegradation of hydrolyzed polyacrylamide under anaerobic and aerobic conditions[J]. *Bioresource technology*, 2016, 216:95-104.
- [13] Zhao C, Zhou J, Yan Y, et al. Application of coagulation/flocculation in oily wastewater treatment: A review[J]. *Science of The Total Environment*, 2020:142795.
- [14] Vengosh A, Jackson R B, Warner N, et al. A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States[J]. *Environmental science & technology*, 2014, 48(15):8334-8348.
- [15] Song Xuefeng, Wu Yueqiang, Xu Chengjun, et al. Research on strong alkali ternary composite flooding produced water treatment process[J]. *Oil & Gas Field Environmental Protection*, 2019, 29(03):4-8+60.
- [16] *Oil & Gas Field Surface Engineering*, 2021, 40(12):39-45.
- [17] Gu Wenge, Chen Zhongxi, Zhao Qiushi, et al. Daqing Oilfield ternary composite flooding produced water treatment technology[J]. *Industrial Water & Wastewater*, 2018, 49(02):48-53.
- [18] Ao Lu, Guo Liang, Wang Fei, et al. Electrochemical-ultrafiltration combined advanced treatment of ternary composite flooding produced water[J]. *Petroleum and Chemical Equipment*, 2021, 24(02): 103-106.
- [19] Gao Zhiyi, Zhao Ruijun, Han Mei, Wang Yimou, Li Peng, Zhao Ruiyu, Liu Chenguang. Research progress on electrochemical treatment of oily wastewater[J]. *Applied Chemical Industry*, 2022, 51(03):841-845.
- [20] Kan Lianbao, Duan Hui, Ding Siqi, Wang Meng, Cui Hongmei. Application and prospect of electrochemical technology in organic wastewater treatment[J]. *Contemporary Chemical Industry*, 2016, 45(05):952-953+956.
- [21] Application of ceramic membrane ultrafiltration technology in sewage reinjection of offshore platform[J]. *Water Treatment Technology*, 2017, 43(10):122-123+127.
- [22] Zhang Dawei, Chen Zhongxi, Ren Lu, Meng Xiangchun, Gu Wenge. Study on Properties and Stability Mechanism of Ternary Composite Flooding Produced Water[J]. *Oil & Gas Chemicals*, 2020, 49(01): 104-111.