Optimization of Pretreatment Technology for Produced Water in Gas Field

Zhirong Ma[1,*], Shouli Zhu[1], Junyi Fu[2]
[1]Karamay Vocational and Technical College, Karamay 834000, China
[2]Petroleum Xinjiang Oilfield Oil and Gas Storage and Transportation Branch, Karamay 834000, China
*Corresponding email: mma0405@sina.com

Abstract

In view of the problems of low overall operation efficiency, serious corrosion of methanol recovery system and obvious sludge blockage in water injection pipeline, the pretreatment technology of produced water in gas field treatment plant has been optimized and improved. By prolonging the settling time of produced water in the unloading tank and raw water tank, the oil and water in the produced water are fully stratified, and an emulsifier is added when necessary to separate the oil from the produced water. In winter, heat tracing is added to the pipe mixer or the outer wall of the reactor tank, or a heated pipe mixer is installed to properly heat the liquid, and the produced water is fully and evenly mixed with the medicament, giving full play to the medicament effect, preventing the flocs from precipitating too quickly, thus improving the settlement effect. The relevant process optimization and improvement measures are put forward to provide reference for the pretreatment process of produced water.

Keywords

Produced water, Water treatment, Mixer, Water analysis

Introduction

In the process of natural gas exploitation, with the continuous development of gas fields, the pressure of gas reservoir decreases, and formation water gradually soaks into the gas reservoir and is produced together with natural gas. At the same time, to increase natural gas production, many drainage gas production processes are used in gas fields, which makes the produced water output of gas fields increase sharply. Because natural gas and water are easy to form hydrate, in the natural gas gathering and transportation system, the flow area of the pipeline is reduced, and the pipeline is blocked [1]. To inhibit the formation of hydrate and reduce the freezing point of hydrate, organic inhibitors are usually injected into natural gas production wellhead or gathering pipeline, and methanol is the most used one. The methanol injected into the pipeline is mixed with natural gas, filtered and separated by the gas gathering station, and then the alcohol-containing sewage in the gas field is produced.

The water produced from gas fields has the characteristics of complex composition and many kinds of impurities through the whole process from natural gas gathering to primary processing [2]. The composition of produced water from gas fields in different regions and seasons is different. Because the produced water absorbs carbon dioxide and hydrogen sulfide in natural gas, it is acidic and contains a lot of suspended solids, condensate oil, minerals and mechanical impurities, which are corrosive to pipelines and equipment [3,4]. If it is not pretreated, it will make the operation of the methanol recovery distillation column difficult, and the qualified rate of methanol production is low. At the same time, it will lead to pipeline corrosion, equipment blockage, scaling, unstable operation of the device and other problems.

When the wastewater at the bottom of the tower is reinjected with high alcohol content, it will pollute the environment. To reduce the cost of gas production and the pollution of methanol to the environment, methanol in produced water is recycled, so it is necessary to carry out a series of comprehensive treatment of produced water in gas fields [5].

Produced water pretreatment status and existing problems

Present situation of pretreatment of produced water

Pretreatment of produced water in gas field refers to the process from the discharge of produced water in gas field to the unloading pool by sewage truck to the methanol recovery unit, which is a physical and chemical process to mainly remove condensate oil, solid impurities and ions that cause corrosion and scaling of equipment and pipelines in produced water [6,7]. The specific process is as follows: the produced water from the gas field is transported from the gas gathering station to the natural gas treatment plant, and first enters the unloading pool, where it is settled, and the oil and water are separated initially, and the dirty oil enters the underground rotating oil tank. The sewage is transferred to the raw water tank by the sewage lift pump and allowed to stand for 12 hours to effectively stratify the oil and water for secondary oil-water separation. The sewage is discharged to the underground rotary oil tank again through the oil discharge pipeline, and the sewage is transferred to the raw water tank by the rotary water pump. In the process of water transfer, the raw water is heated by the steam-water mixing heater to about 25-30℃ and then injected into the pressure degreaser for oil-water separation. The dirty oil enters the underground rotary oil tank, and the degreased sewage and drugs (PH regulator, coagulant and hydrogen peroxide) enter the reaction tank through the pipeline mixer to be fully mixed, and then the coagulant aid and flocculant are added. After the sewage and drugs react, they enter the raw water tank for flocculation and sedimentation, and the produced water after removing mechanical impurities and dirty oil is sent to the methanol recovery device for rectification and separation through the feed pump. In this process, the dirty oil entering the underground rotary oil tank is transported to the crude oil storage tank by the rotary oil pump, and the condensate stabilization device becomes the finished condensate [8]. As known Figure 1.

Figure 1. Pretreatment process of produced water in natural gas treatment plants.

Existing problems

Although the produced water pretreatment system, methanol rectification recovery system and reinjection system of natural gas treatment plant can operate normally at present, the overall operation efficiency is not high, the equipment and pipelines of methanol recovery unit are seriously corroded, and the sludge blockage of water injection pipeline is obvious. After on-site maintenance, it is found that the above problems are directly related to the poor pretreatment effect of produced water [9].

(1) At present, the composition and properties of produced water in gas field have changed greatly compared with the initial stage of production, and the pretreatment process of produced water has never been optimized, so it is urgent to analyze the composition and properties of produced water at present, understand the current water quality characteristics, and develop matching water treatment technology.

(2) The temperature difference in the area where the treatment plant is located is large throughout the year, and the methanol content fluctuates between 20% and 50% at different temperatures. However,

the same dosing scheme is used throughout the year which fails to give full play to the effect of the chemicals. Especially in the case of low temperature and high methanol content in winter, the original dosing process has poor flocculation and sedimentation effect on impurities and low clarity of water quality. Based on water quality analysis and scaling mechanism analysis, it is necessary to carry out reagent optimization tests and optimize dosing measures in different seasons and methanol concentrations, including reagent types, dosage, reaction time and dosing sequence. By analyzing the residual iron content, light transmittance, oil content and other indicators, the effect of dosing was investigated [10].

(3) Due to the poor pretreatment effect of produced water, the equipment pipeline of methanol regeneration unit is blocked and corroded. Therefore, it is necessary to analyze the scale, to find out the reasons for the blockage and corrosion of equipment pipelines and reduce the blockage and corrosion of equipment pipelines by improving the treatment effect of produced water.

(4) Because the produced water quality fluctuates greatly, the original dosing system does not match the existing water quality, the pretreatment effect is not good, and the settling time of the produced water in the raw water tank is insufficient. It is necessary to determine the reasonable settling time, adjust the oil discharge level of the tank, optimize the production system, and optimize the process flow to improve the overall operation effect based on the optimization study of chemicals [11]. According to the requirements of the Gas Field Water Reinjection Method, the oil content in the reinjection water obtained from the gas field produced water after treatment is ≤ 30mg/L and the mechanical impurity is ≤ 15 mg/L; In addition, other control indicators are generally: transmittance ≥ 98%, pH=7~7.5, Fe2+/(mg L-1)≤0.5 mg/L.

Pipeline mixer improvement

On-site pipeline mixer

The “pipeline mixer” is a section of pipeline equipped with turbine blades. When the liquid passes through the pipeline mixer, the built-in blades will rotate to fully mix the flowing liquid. In the dosing process of the pretreatment process of the produced water in the gas field of the natural gas treatment plant, a pipeline mixer is used to mix the chemicals and the gas field sewage. After pressure decreases, the alcohol-containing sewage in the gas field is mixed with sodium hydroxide, hydrogen peroxide and flocculant in turn in the “pipeline mixer”, and then the liquid enters the conical reaction tank to be mixed again. When it is discharged, the coagulant aid is added, passes through the pipeline mixer and the conical dosing mixer, and finally enters the raw material tank (settling tank) for sedimentation. Because of the low field temperature in winter, floc is suspended in water and difficult to settle to the bottom of the tank, which leads to poor settling effect and turbid water quality, which affects the subsequent methanol rectification process [12]. In summer, the settling effect is much better, which may be due to the low temperature in winter, which leads to the rapid flocculation process of impurities such as iron hydroxide, and the floc particles are small and evenly distributed in the water body, thus making it difficult to settle. Therefore, to improve the settling effect in winter, it is suggested to increase heat tracing at the pipeline mixer and reaction tank or install a hearable pipeline mixer to properly heat the liquid to prevent floc from precipitating too quickly, thus improving the settling effect. Therefore, it is necessary to investigate the types of pipeline mixers on the market at present and make suggestions on the selection of pipeline mixers on site.

Pipeline mixer investigation

Natural gas produced water contains a lot of impurities and harmful substances. If it is directly discharged, it will pollute the environment. Therefore, some industrial treatment should be carried out to reduce the pollutant content in the waste and then discharge it. The commonly used method is chemical precipitation.

However, due to the continuous industrial

production, the sewage and chemical reagents are unevenly mixed, and the reaction is incomplete during the settlement. Therefore, the mixed reactor is introduced, which can make the chemicals and sewage react more fully and make the sewage treatment better. It is found that the flocculation is rapid at low temperature, which makes the floc particles small and difficult to settle, so the sewage treatment effect is poor. Therefore, the mixed reactor with heat transfer can be used on this basis, which can make the water treatment achieve better results at low temperature. In this paper, the types and characteristics of commonly used mixing reactors are reviewed [13].

Pipeline mixer is the equipment for mixing raw materials to make them react chemically, which can be divided into dynamic mixer and static mixer. Because the static mixer has the advantages of high efficiency, small size, low energy consumption, easy continuous production, many specifications, wide application range, etc., the industrial pipeline mixer generally refers to the static mixer. The static mixer can be installed horizontally or vertically according to specific requirements, and the dosing pipeline in front of the mixing unit can be designed by users themselves. The mixing efficiency of chemicals can reach more than 90%, which is of great significance to improve the sewage treatment effect [14].

(1) Structure

The static mixer is generally composed of three mixing units, and each mixing unit is a fixed spiral blade twisted by 180 degrees, which is divided into left-handed and right-handed types. The spiral blades in the adjacent two units rotate in opposite directions with a difference of 90 degrees, so that the medicine is fully mixed due to collision when flowing in the pipeline.

(2) Working principle

Static mixer mainly depends on the special structure of internal mixing unit, so that the flow direction of the fluid in the pipeline can be continuously changed, and different fluids can be continuously and efficiently diffused in the pipeline, thus achieving the purpose of mixing.

(3) Types and characteristics

There are many types of static mixers, the materials of which can be UPVC, FRP, carbon steel lining rubber, stainless steel, etc. Among them, the mixer made of UPVC is light in weight, low in price and strong in pressure resistance, while the mixer made of stainless steel is heavier and more expensive. Compared with others, the static mixers made of FRP are relatively poor in pressure resistance. There are various types of static mixers commonly used abroad, such as Keni's, ISG, SMX, SML, BKM, Hi, etc. Aiming at the mixing and reaction process that needs to be heated or cooled, a new static mixer has been developed, which can be divided into two categories. First, a jacket is added to the original static mixer, and a cooling liquid is added to the jacket or heated; Secondly, the insert in the tube, that is, different mixing units are installed in the tubes of the shell-and-tube heat exchanger to exchange heat [15].

S series static mixer. According to its internal structure, S series static mixers can be divided into SV type, SX type, SK type, SL type and SH type. Among them, SV-type internal corrugated, which makes the fluid flow in the tube in a Z shape. After the fluid flows into the mixer, the corrugated plates will cut the fluid and make the fluid fully mixed. SV-type static mixer has the best mixing effect in this series, which is suitable for the mixing, emulsification, reaction and heat transfer enhancement of fluids with viscosity ≤ 102cP, but not for the mixing of gases and high-viscosity liquids. SX static mixer is composed of cross bars, which mainly mix fluids by cutting and shearing, and the mixing effect is inferior to SV static mixer. It is suitable for mixing and reaction process with viscosity ≤104cP and has good effect when the throughput is large. SK-type single spiral static mixer mainly mixes fluids by rotating and cutting fluids.

It is suitable for mixing fluids with viscosity ≤ 106cP in petroleum, chemical and pharmaceutical fields, but the mixing effect is poor compared with

SV-type static mixer. SL type is suitable for mixing fluids with 106cP viscosity and can heat the circulation at the same time. SH-type is composed of double channels, and spiral blades are placed in the channels, which have high processing accuracy and are suitable for clean media with small flow and high mixing requirements.

The specifications of the static mixer can be selected according to the requirements, and the parameters such as the model, material, nominal diameter and pressure of the mixer should be made clear when selecting. On some occasions, because the temperature is too high or too low, the reaction process needs to absorb heat or release heat. To solve one of the problems, the static mixer is jacketed. For example, the HYVF mixer produced by Qidong Hengye Petrochemical Metallurgical Equipment Co., Ltd. is a jacket mixer, and the size and specifications can be selected according to your own needs.

HTF type enhanced heat transfer mixing reactor. Its internal structure is like that of static mixer, which can fully mix the fluids. There are thin tube bundles inside, which can be filled with cold/hot exchange media, which can not only play the role of mixing, but also provide a large heat transfer specific surface area. HTF-I type enhanced heat transfer mixing reactors can be directly connected to the pipeline without being combined with other fittings, which has good effect on mixing and heat transfer of high viscosity fluids. The HTF-I model is especially suitable for polymerization reactors, which can make the fluids entering the pipeline mix well and strengthen the heat transfer process.

Other types of mixers. In addition to the commonly used mixers listed above, there are some other types of mixers, such as SK-type and SL-type tubular heat exchangers, JLF-type static mixer heat exchangers, etc., which are used in the mixing, dissolution and reaction process of heat exchange occasions. SK-type and SL-type shell-and-tube heat exchangers are units with SK-type or SL installed in the tubes of shell-and-tube heat exchangers, which will form a structure in which many SK-type static mixers are connected in parallel, so that material mixing and heat transfer can be achieved at the same time during use.

(4) Application of static mixer

Application of static mixer in petrochemical industry. Static mixers are mainly used in petroleum blending, crude oil desalination and dewaxing, extraction and other processes. The blending of oil products mainly includes fuel oil blending, lubricating oil blending and asphalt blending, that is, the characteristics of petroleum products (such as density, octane number, cetane number, etc.) are blended according to national standards to make them meet the standards. Compared with the original mechanical stirring method, the pipe mixer is introduced into asphalt blending, and its mixing effect is better. Wax content is an index to evaluate crude oil. Using static mixer to separate oil wax has the advantages of high efficiency and low energy consumption. The salt content in Jianghan Oilfield is as high as 16×104mg/L, and it is reduced to 188mg/L after using the static mixer, so it can be concluded that the mixer has a good effect in crude oil desalination. In the process of extraction, it is difficult to mix the two phases. The mixer can fully mix the two phases and improve the extraction efficiency. After the static mixer was used to replace the Venturi tube in the refinery of Gao Qiao Petrochemical Company, the oil yield was improved, and the energy consumption was reduced.

Application of static mixer in the medical field. In the field of medicine, pipeline mixers can be used for mixing, emulsification, extraction, chemical reaction and other processes. In medicine, static mixers are used to mix liquids that are not miscible with each other, especially fluids with high viscosity. Xiao linjiu compared the static mixer with the traditional kettle reactor in nitrification experiment, and the energy consumption was reduced by 33%~50%. Because the static mixer has good sealing performance, it is suitable for toxic, flammable and other dangerous reactions with high safety factors. Application of static mixer in the field of environmental protection.

Wastewater is one of the main factors that pollute the environment. When treating wastewater, some solvents such as flocculants and coagulant AIDS will be added. At the initial stage, the mechanical stirring method will be used. Because of the poor treatment effect due to uneven mixing, the effect will be obviously improved after using the mixer. Polyalanine chloride is a commonly used flocculant for treating wastewater. Because of the small particles in the flocculation process, coagulant AIDS will be added, and polyacrylamide is commonly used. After investigation, Shanghai Yizhong Textile Company used SVL static mixer to treat wastewater. Phenol-containing wastewater will be produced when diphenyl carbonate is produced in Shanghai No.2 Dyeing and Chemical Plant. In wastewater treatment, the static mixer is used instead of the pulse extraction tower, the wastewater treatment capacity is increased from 12t/d to 30t/d, and the phenol content of water is reduced from 523.3mg/L to 43.3mg/L, which has achieved good results.

Optimization and improvement of on-site pipeline mixer

Based on the literature and market research of "pipeline mixer", it is suggested that the treatment plant should install a heating device on the original pipeline mixer or replace it with a heated pipeline mixer. The following types of pipe mixer can be considered:

(1) Static mixer. The static mixer can be installed horizontally or vertically according to specific requirements, and the dosing pipeline in front of the mixing unit can be designed by users themselves. The mixing efficiency of chemicals can reach more than 90%, which is of great significance to improve the sewage treatment effect.

(2) HYVF mixer. On some occasions, because the temperature is too high or too low, the reaction process needs to absorb heat or release heat. To solve this problem, a jacket mixer is put based on the original static mixer. For example, the HYVF mixer produced by Qidong Hengye Petrochemical Metallurgical Equipment Co., Ltd. is a jacket mixer, and the size and specifications can be selected according to your own needs.

(3) HTF type enhanced heat transfer mixing reactors.

Produced water pretreatment process optimization and suggestions

Take the following control measures for effective treatment:

(1) Extend the settling time of the produced water in the unloading tank and the raw water tank, so that the oil and water in the produced water can be fully layered, and if necessary, add demulsified to further separate the oil.

(2) Through water quality analysis, it was found that the pH value of the reaction tank did not reach the expected 7.5. There are two possibilities for this result, one is insufficient NaOH addition, and the other is uneven mixing of raw water and reactant. In view of this problem, it is suggested that the dosing system should be strictly implemented, and the pH value of water quality should be detected regularly. Because the produced water and the reagent can't be fully mixed, it is suggested that the vertical reaction tank should be replaced by a multi-stage vortex reaction settling tank. The vortex reaction settling tank adopts a multi-stage vortex mode, and the number of micro-vortexes increases through the multi-stage vortex in the tank, which greatly increases the collision times of various particles, which is conducive to the full mixing of the produced water and the reagent. Through micro-vortex coagulation and three-dimensional contact flocculation, the reaction rate and flocculation efficiency can be greatly improved.

(3) Strictly ensure the flocculation and sedimentation time of dosing, so that the produced water can be fully flocculated and precipitated in the raw water tank.

(4) Because the iron ion content in the produced water is less, the iron removal rate can be improved by optimizing the reaction temperature, stirring rate, settling time, dosing sequence and dosage.

(5) In winter, heat tracing is added to the pipeline mixer or reaction tank, or a hearable pipeline mixer

is installed to properly heat the liquid, to prevent floc from precipitating too quickly, thus improving the settling effect.

Conclusion

The vertical reaction tank is replaced by multi-stage vortex reaction settling tank, which further enhances the mixing effect of produced water and chemicals (the vortex reaction settling tank adopts multi-stage vortex mode and passes through multi-stage vortex in the tank, so that the number of micro-vortexes is increased and the collision times of various particles are greatly increased, which is conducive to the full mixing of produced water and chemicals). Through micro-vortex condensation and three-dimensional contact flocculation, the reaction rate and flocculation efficiency can be greatly improved.

Funding

This work was not supported by any funds.

Acknowledgements

The authors would like to show sincere thanks to those techniques who have contributed to this research.

Conflicts of Interest

The authors declare no conflict of interest.

References

[1] Su, B, Huang, L., Li, S., Li, X. (2018) Optimization of pretreatment process parameters of alcohol-containing wastewater in gas fields. *Petrochemical Application*, 37(11), 21-24.

[2] Wang, L., Wang, C., France. (2018) Study on treatment technology of OD-MBR biofilm in produced water of low permeability oilfield. *Petroleum and Chemical Equipment*, 21(8), 103-105.

[3] Wang, T. (2018) Adaptability analysis of produced water treatment process in Qinghuabian Oil Production Plant. *China Water Supply and Drainage*, 34(7), 85-88.

[4] Huang, X., Hao, J., Ge, X. (2017) Discussion on defoaming methods of volatile phenol pretreatment in gas field produced water. *Environmental Protection of Oil and Gas Fields*, 27(5), 54-56+62.

[5] Lu, Z., Gao, P., Ma, C., et al. (2015) Water pollution from shale gas production and progress in treatment technology. *Natural Gas and Petroleum*, 33(6), 90-95+14.

[6] Wang, N., Zhang, K., Zhao, L., Xu, D., Zhao, X., Ma, L. (2014) Standardization of operation parameters of gas field produced water treatment device. *Petrochemical Application*, 33(7), 110-113.

[7] Zhu, Y., Ma, P., Guo, L. (2017) Membrane separation technology and its application. *Contemporary Chemical Industry*, 46(6), 1193-1195+1199.

[8] Kan, L., Duan, H., Ding, S., et al. (2016) Application and prospect of electrochemical technology in organic wastewater treatment. *Contemporary Chemical Industry*, 45(5), 952-953+956.

[9] Saritha, V., Srinivas, N., Srikanth Vuppala, N. V. (2017) Analysis and optimization of coagulation and flocculation process. *Applied Water Science*, 7, 451-460.

[10] Vashisth, V., Nigam, K. D. P., Kumar, V. (2021) Design and development of high shear mixers: Fundamentals, applications and recent progress. *Chemical Engineering Science*, 232, 116296.

[11] Di, T., Sun, X., Chen, P., Huang, Q., Liu, X. (2024) A novel static mixer for blending hydrogen into natural gas pipelines. *International Journal of Hydrogen Energy*, 86, 1118-1128.

[12] Lei, H., Guan, X., Sun, Y., Yan, H. (2022) A novel design of in-line static mixer for permanganate/bisulfite process: Numerical simulations and pilot-scale testing. *Water Environment Research*, 94(5), e10725.

[13] Aragaw, T. A., Bogale, F. M., Aragaw, B. A. (2021) Iron-based nanoparticles in wastewater treatment: A review on synthesis methods, applications, and removal mechanisms.

Journal of Saudi Chemical Society, 25(8), 101280.

[14] Frison, L., Gumbel, U., Steiger, S., Sinnesbichler, H., Ahrens, B., Lottis, D., Cadenbach, A. M. (2024) Presentation of a distributed testing infrastructure for joint experiments across multiple remote laboratories for robust development of new district heating concepts. *Smart Energy*, 15, 100152.

[15] Li, C. G., Liu, C., Xu, W. H., Shan, M. G., Wu, H. X. (2022) Formation mechanisms and supervisory prediction of scaling in water supply pipelines: A review. *Water Research*, 222, 118922.