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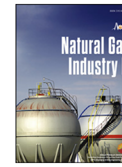

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Research Article

New progress in wastewater treatment technology for standard-reaching discharge in sour gas fields[☆]

Yang Jie[a,*] & Xiang Qigui[a,b]

[a] *HSE and Technical Supervision Research of PetroChina Southwest Oil & Gas Field Company, Chengdu, Sichuan 610041, China*
[b] *National Energy R&D Center of High Sulfur Gas Reservoirs Exploration, Chengdu, Sichuan 610213, China*

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Abstract

Gas field water is generally characterized by complex contaminant components and high salinity. Its proper treatment has always been the great concern in the field of environmental protection of oil & gas fields. In this paper, the wastewater from a gas field in the Sichuan Basin with high salinity and more contaminants (e.g. sulfides) was treated as a case study for the standard-reaching discharge. Lab experiments were carried out to analyze the adaptability and effectiveness of coagulation–desulfurization composite treatment technology, chemical oxidation based ammonia nitrogen removal technology and cryogenic multi-efficacy distillation technology in the treatment of wastewater in this field. The results show that the removal rate of sulfides and oils is over 90% if polymeric ferric sulfate (PFS) is taken as the coagulant combined with TS-1 desulfurization agent. Besides, the removal rate of ammonia nitrogen is over 96% if CA-1 is taken as the oxidant. Finally, after the gas field water is treated by means of cryogenic three-efficacy distillation technology, chloride concentration of distilled water is below 150 mg/L and COD_{cr} concentration is less than 60 mg/L. It is concluded that after the whole process treatment, the main contaminant indicators of wastewater in this case study can satisfy the grade one standard specified in the Integrated Wastewater Discharge Standard (GB 8978–1996) and the chloride concentration can meet the requirement of the Standards for Irrigation Water Quality (GB 5084–2005). To sum up, the above mentioned composite technologies are efficient to the wastewater treatment in sour gas fields.

Keywords: Sulfide-bearing gas field water; Coagulation; Desulfurization; Chemical oxidation; Standard discharge; Ammonia nitrogen; Chloride; Cryogenic multi-efficacy distillation; Sichuan Basin

Gas field water is mainly composed of free water and condensate water. Free water is generally characterized by high salinity and presence of sulfides, while condensate water has low salinity. The common treatments for gas filed water include deep well reinjection, standard-reaching discharge, etc. At present, the wastewater treatment methods for standard-reaching discharge in gas fields mainly include flash desulfurization, coagulating sedimentation, thermal/membrane desalination and biochemical treatment methods [1–5]. The flash desulfurization needs a lot of alkali liquor to reabsorb the removed hydrogen sulfides. The conventional coagulating sedimentation cannot effectively remove the ammonia nitrogen in gas field water, thus leading to some problems such as more contaminants (e.g. ammonia nitrogen) in the fresh water produced from the demineralization equipment exceeding standard. The application of the biochemical treatment of gas field water is often challenged by microbes susceptible to toxicity inhibition, poor load and shock resistance ability, low removal rate of complex organic matter in water, and etc. In this paper, the authors conducted lab experiments on gas field water treatment technology for standard-reaching discharge and discussed the optimization of relevant technical

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* Corresponding author.
E-mail address: 16696952@qq.com (Yang J.).
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parameters, with the gas field water produced from marine carbonate gas reservoir in the Sichuan Basin as example, which is characterized by high salinity and presence of sulfides, ammonia nitrogen, and complex organic matters. In this study, the coagulation−desulfurization integration technology and the ammonia nitrogen removal technology by physical chemistry method are adopted as pretreatment processes, and the cryogenic multi-efficacy distillation technology is selected for desalination and deep treatment [6−13].

1. Experimental materials and methods

1.1. Experimental materials

Experimental materials and reagents include desulfurization agent TS-1, coagulant (PAC-1, PAC-2, PAFC-1, PAFC-2 and PFS), HPAM and ammonia nitrogen removal agent CA-1. Gas field water was taken from a gas field in the Sichuan Basin and the main contaminant characteristics and analysis methods are shown in Table 1. Instruments and equipment include coagulation tester, mechanical stirrer, pH meter, vacuum distillation experimental equipment and analytical balance.

1.2. Experimental methods

1.2.1. Coagulation−desulfurization process

In view of the sulfur characteristics of gas field water, oxidized desulfurization agent TS-1 was selected for desulfurization treatment experiment. In the early stage of experiment, the removal rate of sulfides rose obviously with the increase of dosages of desulfurization agent; when the dosage exceeded 80 mg/L, the removal rate of sulfides did not obviously rise any more. Accordingly, the dosage of the desulfurization agent TS-1 was set at 80 mg/L. Meanwhile, the dosage of the coagulant HPAM was set at 5 mg/L, 10 mg/L, 20 mg/L and 30 mg/L respectively by referring to the common dosage range of the coagulants for wastewater treatment. Then, the influence of dosage on the treatment effect was studied. It is found that the flocculating constituents had good quality and the sedimentation time was shortest under the condition of coagulant dosages at 20 mg/L. So the dosage of the HPAM was set at 20 mg/L.

Table 1
Gas field water quality characteristics and analytical method.

Water quality index	Numerical value	Analytical method
COD_{cr}/(mg·L $^{-1}$)	400−600	Dichromate method
Oils/(mg·L $^{-1}$)	10−20	Infrared spectrophotometry
Sulfides/(mg·L $^{-1}$)	100−150	Iodimetry
Ammonia nitrogen/(mg·L $^{-1}$)	60−90	Nessler's reagents spectrophotometer
SS/(mg·L $^{-1}$)	50−80	Gravimetric method
Chloride ion content/(mg·L $^{-1}$)	5×10^4−6×10^4	Nitrate titration method
Total salinity/(mg·L $^{-1}$)	8×10^4−10×10^4	Gravimetric method
pH value	5−6	Glass electrode method

Given the above dosages, PAC-1, PAC-2, PAFC-1, PAFC-2 and PFS were selected for comparison. When the coagulant is determined, its dosage and the pH value of gas field water were adjusted for the coagulation−desulfurization experiment in order to optimize the technical parameters.

1.2.2. Ammonia nitrogen removal process

The medicament oxidation method was selected for ammonia nitrogen removal. The raw gas field water contains a high content of sulfides. If the ammonia nitrogen removal is carried out before the sulfides are removed, such sulfides must consume a great quantity of oxidant, leading to a higher treatment cost. Meanwhile, the suspended matters and oil contaminants in the raw water would reduce the efficiency of ammonia nitrogen removal. Therefore, ammonia nitrogen removal should be carried out after the coagulation−desulfurization treatment.

CA-1 was selected as the treating agent to degrade the ammonia nitrogen in the gas field water after the coagulation−desulfurization treatment. In the treated gas field water, the content of contaminants (e.g. sulfides and suspended matters) was very low and had small influence on the effect of ammonia nitrogen removal. The dosage of CA-1, pH value of gas field water and the influence of reaction time on the removal effect were investigated respectively.

1.2.3. Deep treatment process of gas field water by cryogenic multi-efficacy distillation

Three-efficacy decompression distillation technology was selected for desalination and deep treatment of gas field water. By using vacuum distillation units, the validity of the whole process of gas field water treatment was verified under different pressures.

2. Results and discussion

2.1. Coagulation−desulfurization process and condition optimization

2.1.1. Selection of efficient coagulants

The PH value of gas field water was regulated to 8 and the dosages of desulfurizer TS-1 and coagulant HPAM were fixed. PAC-1(1), PAC-2(2), PAFC-1(3), PAFC-2(4) and PFS (5) were selected for comparative experiment, with removal rates of COD and sulfides as the screening index. The experimental results are shown in Fig. 1.

It can be seen in Fig. 1 that, among the five coagulants, PFS performs the best in removing contaminants in the gas field water, with a COD removal rate of 32.7% and a sulfides removal rate of 79.5%. Analysis suggests that sulfate in PFS can form with high-concentration calcium and magnesium ions in the gas field water into insoluble flocs; as a result, the alum blossom formed by PFS has a higher density and can more effectively adsorb and sweep the contaminants. Furthermore, Fe^{3+} is able to oxidize and remove partial sulfides with a high redox potential, making PFS function well in