Effect of NTP Pretreatment on Thermal Resistance and Fouling Components of Oilfield Wastewater

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Abstract. In order to prevent scaling in the process of oilfield wastewater evaporation, low temperature plasma is used for pretreatment of heavy oil wastewater. It reacts with the ions and radicals produced by the low-temperature plasma and then is send into the evaporator. The changes of various indexes of the distilled water and the distribution of fouling in the evaporation process of heavy oil wastewater after plasma pretreatment were studied. The results showed that the content and hardness of silica in wastewater were decreased after plasma pretreatment, which was more suitable for evaporation treatment. At the same time, the content of salt and oil in distilled water is reduced, and the quality is improved. In addition, when the steam concentration was 30–40 times, the suspended solids in the concentrated solution of the wastewater increased significantly after the plasma treatment. Correspondingly, the fouling at the bottom of evaporator is greatly reduced. Comparing the various indexes of distilled water and the feed water index of gas injection boiler, it can be seen that the excessive oil content in distilled water is the biggest obstacle to the recovery of distilled water to boiler feed water. Low temperature plasma pretreatment can provide a quick and new way to solve the scaling problems and water quality problems in the recovery of distilled water from a large number of heavy oil wastewater.

1. Introduction
At present, most of the oil fields in China have entered the middle and late stage of oil exploitation. The water content of the crude oil has reached 70% - 80% [1-2]. Some of the oilfields are even up to 90%. With the increase of the water content of the produced fluid, the waste water of the produced liquid needs to be increased rapidly [3]. Heavy oil wastewater refers to the water discharged from oil and water separation after treatment of heavy crude asphalt petroleum (heavy oil) production fluid. Its water quality is characterized by high water temperature, large oil content, large viscosity of sewage oil and serious emulsification [4]. The main pollutants in heavy oil wastewater are petroleum, suspended solids, sulfide, volatile phenols, chloride, fluoride, ammonia nitrogen, saprophytic bacteria and sulfate reducing bacteria. It has a certain degree of hardness and salinity. Because of the high oil content, high salt content and heavy composition of the heavy oil wastewater, the membrane treatment method lacks the long-term effective pretreatment process, so that the heavy oil wastewater treatment is very expensive. As the heavy oil wastewater has a high temperature, the use of chemical treatment will waste a lot of waste water waste heat [6-8]. The evaporation process has little requirement for water quality. Through a
certain pretreatment, it can be directly into the evaporation equipment. Even if the high oil-containing wastewater enters, it will only affect the efficiency of the evaporation system in a short time without affecting the normal operation of the entire system. In addition, evaporation process can utilize the heat energy of heavy oil wastewater. With the increase of wastewater temperature, the heat transfer area of evaporator decreases [5]. For the heavy oil wastewater with relatively high temperature, evaporation process can make more effective use of waste heat of wastewater. A large number of heavy oil wastewater cannot be discharged into the environment, and a large number of high-quality water sources are needed to supply the boiler feed water [11-13]. However, the evaporation process can treat oilfield wastewater for high quality boiler feed water, which can be used as a good resource recycling model [14]. Due to the high content of silicon in the heavy oil wastewater, there is still a residue even after the silicon removal process [9]. During the evaporation process, the silicon scale will be very difficult to handle, which seriously affects the evaporation efficiency and the use of the evaporation equipment [15].

2. Experimental device
The experimental setup consists of two parts: the NTP preprocessor and the evaporative condensed distilled water. Heavy oil wastewater first enters the direct-current (DC) high pressure narrow pulse NTP generator for pretreatment. After pretreatment, the water samples were collected and evaporated and condensed to obtain distilled water and a small amount of residual concentrated liquid. The quality of distilled water and concentrated liquid were detected respectively. The plasma machine is a DC narrow pulse type with a peak voltage of 30K V. The energy of single discharge is 2 joules / times. The pulse discharge frequency can be adjusted between 0~1000 /s. During the experiment, the flow was atomized by the nozzle group and then entered the plasma cylinder [10]. The amount of water handled per hour is 6 t. Therefore, when the discharge frequency is 1000 times / s, tons of electricity consumption is only 0.333 kW · h. No reagent was added in the experiment. The treated wastewater is pumped back to the storage tank and sprayed into the plasma tube again. The treated water is evaporated and then condensed with an evaporator. After the steam is heated and evaporated, the steam is recovered by the condenser. Treatment process of oilfield wastewater evaporation process is shown in Figure 1.

![Figure 1. Treatment process of oilfield wastewater evaporation process](image)

3. Experimental method
In the NTP pretreatment experiment, the water was injected into the NTP excited tube after pressure atomization, and the residence speed in the tube was about 0.2 s. The water samples were subjected to cyclic pretreatment at different pulse frequencies. The changes of silica, hardness, heavy metal and oil in water samples treated with different pulse frequency were studied. The appropriate pulse frequency for the treatment of heavy oil wastewater is determined. The number of pulses and the number of cycles are shown in Table 1.
Table 1. The number of pulses and the number of cycles

| Number of plasma pulses and cycles | After plasma pretreatment | Evaporation of distilled water |
|-----------------------------------|---------------------------|-------------------------------|
| A water sample                    | A (original sample)       | A'                            |
| 300 times / s cycle once          | A3001                     | A3001'                        |
| 300 times / s cycle twice         | A3002                     | A3002'                        |
| 500 times / s cycle once          | A5001                     | A5001'                        |
| 500 times / s cycle twice         | A5002                     | A5002'                        |
| 900 times / s cycle once          | A9001                     | A9001'                        |
| 900 times / s cycle twice         | A9002                     | A9002'                        |
| B water samples                   | B (original sample)       | B'                            |
| 900 times / s cycle once          | B9001                     | B9001'                        |
| 900 times / s cycle twice         | B9002                     | B9002'                        |

The original water samples of the heavy oil wastewater and the water samples of the heavy oil waste water pretreated by NTP were respectively evaporated and condensed. The quality of distilled water and concentrated liquid is compared.

4. Results and discussion

4.1. The change of conductivity before and after pretreatment

The pH of the water sample is always weakly alkaline and the pH varies between 9.4 and 9.6. Since the A water sample and the B water sample are taken from different heavy oil fields, the pH of the A water sample is higher than that of the B water sample. The pH values of water samples changed slightly after NTP treatment. For A samples, when the discharge frequency was 300/s and 500/s, the pH value decreased slightly, and it decreased further with the increase of processing times. When the discharge frequency was 900/s, the pH value increased slightly after the cycle. For B samples, the pH value still declined slightly even when the discharge frequency was 900/s.

Compared with the hardness before and after treatment, it can be found that the hardness of two water samples of A and B decreases to less than half of the original hardness after NTP treatment, which will greatly reduce the scaling tendency during evaporation. For group A water samples, the lowest hardness appears at 500 times / s frequency after treatment once. For other cases and water samples of group B, the hardness was further reduced after 2 treatments. Conductivity is the index of water conductivity. When the number of ions in the water is relatively stable, the greater the total ion concentration in water, the greater the conductivity. When the impurity component in the water is more stable, the conductivity can represent the salt content in the water. The greater the conductivity of water, the greater the amount of soluble salt. Table 2 shows the conductivity changes of water samples after treating heavy oil wastewater with different pulse number. The conductivity of the A sample and its NTP-treated water samples changed significantly with the increase in the number of pulses and showed an upward trend in general. This is because NTP treatment, heavy oil wastewater absorbs free radical ions and increases the concentration of ions. B water samples showed a decreasing trend, because the original ion type of B water samples was different. The absorption of free radicals caused by plasma may lead to the precipitation of some ions, resulting in the decrease of conductivity. The water quality of wastewater treated by low temperature plasma is shown in Table 2.
Table 2. Low temperature plasma treatment of water quality

| Water samples | pH value | Conductivity / μS cm⁻¹ | Silica / mg L⁻¹ | Hardness (CaCO₃) / mg L⁻¹ |
|---------------|---------|------------------------|----------------|----------------------------|
| A             | 9.57    | 3440                   | 246.52         | 75.80                      |
| A3001         | 9.5     | 3450                   | 65.21          | 40.11                      |
| A3002         | 9.4     | 3350                   | 53.04          | 36.52                      |
| A5001         | 9.55    | 3500                   | 51.21          | 19.21                      |
| A5002         | 9.46    | 3540                   | 54.25          | 36.10                      |
| A9001         | 9.53    | 3500                   | 53.64          | 32.70                      |
| A9002         | 9.62    | 3660                   | 69.46          | 22.61                      |
| B             | 8.75    | 4940                   | 146.13         | 36.15                      |
| B9001         | 8.66    | 4590                   | 90.76          | 16.86                      |
| B9002         | 8.50    | 4640                   | 95.02          | 11.10                      |

As can be seen from Table 2, after plasma treatment, the dissolved concentrations of silica in A water samples and B water samples were significantly reduced. However, in order to obtain the minimum concentration of silica, there is one of the most reasonable treatment conditions. For group A water samples, the lowest SiO₂ concentration appeared at 500 times /s frequency, and the removal rate of soluble silica reached 80%. For group B, the lowest concentration of silica in water samples was B9001 water sample. NTP treatment can significantly reduce soluble silica in heavy oil wastewater. Similar to the decrease in hardness, it is beneficial to subsequent evaporation treatment and can reduce the tendency of silicon fouling in evaporation equipment.

4.2. The scaling of the evaporation process and the inhibitory effect of NTP pretreatment

After evaporation, all the water samples of the evaporator wall are present in varying degrees of fouling. After plasma treatment, the scaling of water in the evaporation process will also change. It is reflected in two aspects: First, the scale is deposited from the wall of the evaporator, and it is difficult to remove the scale into a precipitate dispersed in the concentrate. Second, in the process of continuous evaporation, due to changes in the wall of the evaporator wall, the evaporator wall and saturated boiling water temperature difference is not consistent. Wastewater A and NTP-treated A3001 and Wastewater B and NTP-treated B9001 were continuously evaporated in the evaporator to nearly 40 times. The concentrated solution was filtered through a microporous filter membrane of 0.45 μm pore size, and the suspension was separated and weighed and dried. The wall of the evaporator is scratched with a hard plastic sheet and then washed with dilute nitric acid. All the washings and dirt are collected. After the evaporation of dry water, the dry matter is weighed to obtain the quality of the dirt remaining at the bottom of the evaporator. The comparison of the mass of suspended solids with dirt is shown in Table 3.

Table 3. The comparison of the mass of suspended solids with dirt

| Water samples | Suspended matter in the concentrate / mg L⁻¹ | Evaporator scale / mg L⁻¹ |
|---------------|--------------------------------------------|--------------------------|
| A             | 18.5                                       | 89.6                     |
| A3001         | 35.4                                       | 77.2                     |
| B             | 30.2                                       | 58.3                     |
| B9001         | 66.6                                       | 32.9                     |

As can be seen from Table 3, after NTP treatment, the quality of the dirt at the bottom of the evaporator decreased. At the same time, the mass of the suspended solids in the concentrate rises. It is
shown that after NTP treatment, the crystallization of the fouling ions migrates from the evaporation surface to the liquid phase.

5. Conclusion
In this paper, the effect of heavy oil wastewater after NTP pretreatment on its evaporation recovery process and its distilled water quality was studied. The conclusions are as follows: After NTP treatment, the pH value of heavy oil wastewater decreased slightly, and the conductivity also changed. The content and hardness of silica decrease by more than half, which is helpful to prevent the formation of fouling during evaporation, and reduce the conductivity and hardness of distilled water. The quality of distilled water produced by different water treatment is different. Other measures should be taken to prevent foam and foam from being carried by steam, so as to improve the quality of distilled water and meet the requirements of steam injection boiler. The pretreatment of NTP can meet the requirement of oil content and SiO₂ content. After NTP pretreatment, the fouling of the heavy oil wastewater is obviously inhibited. The fouling ions are obviously transferred to the liquid phase. After NTP pretreatment, the evaporation and fouling of wastewater is slow, which shows that the difference of temperature difference between evaporator and boiling water rises slowly.

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