

Reclamation of the Polymer-Flooding Produced Water

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Abstract

In order to resolve the discharge problem of the polymer-flooding produced water (PFPW) in crude oil extraction, the PFPW was treated by a four-grade and four-segment (four GS) electro dialysis reversal (EDR) set-up. The testing results show that the treated PFPW has two kinds, one is the diluted treated PFPW, the total dissolved solids (TDS) of the diluted treated PFPW is less than the original PFPW, the diluted treated PFPW is feasible for confecting polymer solution; another one is the concentrated treated PFPW, the TDS of the concentrated treated PFPW exceeds the original PFPW, the concentrated treated PFPW is feasible for replacing the PFPW as the injecting water in the water-flooding process for high permeability layer. This treatment technology can not only decrease environment pollution resulted by the PFPW discharge, but also achieve closed-circuit of the water resource during crude oil extraction by using polymer flooding technology.

Keywords: Polymer-Flooding Produced Water, Total Dissolved Solids, Electro dialysis, Treatment

1. Introduction

In crude oil extraction, water can be injected into the stratum to drive the crude oil out of the ground, which is often termed as water flooding process or secondary oil extraction. The oil content would decrease after the secondary oil extraction is operated for some time. In order to improve the oil recovery, polymer flooding (injected water containing polymer) and alkaline-surfactant-polymer flooding (injected water containing alkaline, surfactant and polymer) would subsequently be used, which is often called as tertiary oil extraction. Industrial experiences show that polymer flooding can enhance oil recovery by up to 12% and plays a key role in the oil exploitation [1,2]. This technology has been widely used in Daqing oilfield in China in recent years [3-5]. Recent statistics show that oil production by polymer flooding in China reached 10×10^6 ton in 2006, and Daqing oilfield has the largest polymer flooding project in the world.

Figure 1 illustrates process of tertiary oil extraction by polymer flooding and treatment of produced water. A large quantity of a polymer (hydrolyzed polyacrylamide, HPAM) is dissolved in water to increase the solution viscosity before water is injected into the stratum

through water wells. The HPAM solution with some crude oil is then extracted from the oil wells. The produced liquid becomes produced water (oily wastewater) after dehydration process using three-phase separators. And the produced water becomes polymer-flooding produced water (PFPW) after it is further treated. The PFPW contains polymer, oil, calcium, magnesium, Carbonate and so on.

After the removal of oil, grease, suspended solids, and organic compounds, the PFPW is our investigative content. There are few effects of HPAM on treatment of PFPW by four GS EDR technology and the effects of HPAM has been described in another paper [6]. The high total dissolved solids (TDS) concentration in produced water still poses a challenge in the treatment for beneficial use. It is well known that there are some corresponding relation between the viscosity and the TDS of PFPW. When TDS is a little higher, correspondingly viscosity is a little lower, vice versa [7]. However viscosity is one of the most important parameters to achieve polymer flooding. Simulated experimental results showed when TDS is less than the one of surface water, whether at the aspect of viscosity or shear-resistance ability, the quality of the PFPW can always meet all the conditions for oilfield polymer solution confection. So we

can think removing TDS is the key problem to actualize the PFPW reused. Separation technologies that are currently available for desalting produced water include filtration with bentonite membrane [8], reverse osmosis [9,10–12], and electro dialysis (ED) [6]. Most of the published work on the removal of TDS from oilfield produced water was addressed with the use of reverse osmosis, few scaled-up tests of electro dialysis has been performed for this application [6]. The reduction of TDS in produced water with ED is the focal point of this paper.

In ED, electrolytes are transferred through a system of solutions and ion-exchange membranes by an applied electric potential gradient. An ED stack consists of cation-exchange membranes, which are permeable to positively charged ions but not to negatively charged ones, and anion-exchange membranes, which are permeable to negatively charged ions but not to positively charged ones. In the stack, cation-exchange membranes alternate with anion-exchange membranes to form solution compartments. When an electrical potential is applied between the electrodes at the end of the stack, all cations in the solution circulating through the stack tend to move toward the cathode and all the anions tend to migrate toward the anode. The cations that migrate through cation exchange membranes toward the cathode are rejected by anion-exchange membranes; simultaneously, the anions that pass through anion-exchange membranes toward the anode are rejected by cation-exchange membrane. As a result, ion depletion and concentration are accomplished in alternating solution compartments. The diluate streams from the alternating compartments are combined and distributed back to the

same compartments to continuously remove the ions from the diluate. An analogous process occurs to continuously increase the ions in the concentrate [13].

In order to reduce the risk of caused scaling by concentration polarization and suspended solids adsorbing, this set-up adopts four-grade and four-segment (four GS) electro dialysis reversal (EDR) technology to desalinate the PFPW. Through the test results, the conductivity of the treated PFPW was under 1.3mS/cm and the energy consumption for producing 1m³ diluted treated PFPW was less than 1kW·h. keeping the flowrate ratio of concentrated and diluted treated PFPW as 1:1, as well as varying the flowrate and voltage, the removal rate under different flowrate was measured. The optimal operating conditions were studied. In optimal conditions, the available uses of the diluted treated PFPW and the concentrated treated PFPW were analyzed.

2. Experiment

The test equipment is shown in Figure 2. This set-up consists of feed water pump, drainage pump, feed water pipes, draining pipes, flowmeters, four GS EDR membrane stack (the active area of a membrane is 400×1600 mm². There are 4 segment membrane stacks. Each segment membrane stack consists of 75 anion-exchange, 76 cation-exchange membranes and 150 spacers which are arrayed alternately), 5 pairs of Ti-Ru electrodes, automatic control cabinet, rectifier cabinet, online conductivity meter, 20kW transformer, air compressor, draining tank and pickling tank.

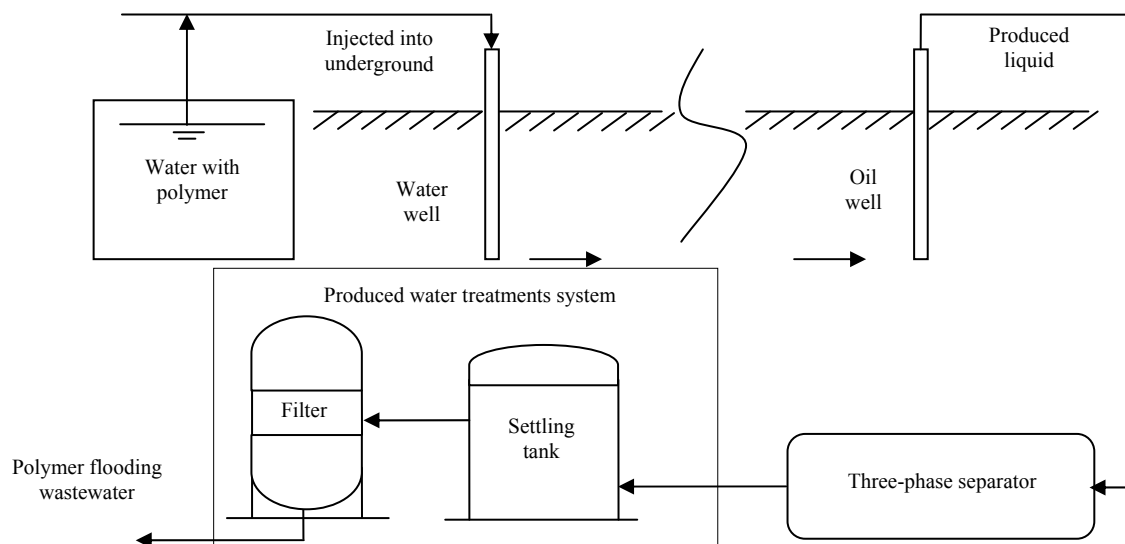


Figure 1. Process of tertiary oil extraction by polymer flooding and treatment of produced water.



Figure 2. Test equipment.

3. Results and Discussion

Firstly, electrical potential difference and feed water were applied in the set-up. Under the condition of adopting four GS electro dialysis reversal technology, keeping the flowrate ratio of concentrated and diluted treated PFPW as 1:1, as well as varying the flowrate and voltage, the removal rate under different flowrate was measured. The results are shown in Figure 3.

Under this operating condition, when the flowrate was $3\text{m}^3/\text{h}$, the minimal removal rate of TDS was 77.4%; the maximal removal rate of TDS was 94.4%. When the flowrate was $4\text{m}^3/\text{h}$, the minimal removal rate of TDS was 75.8%; the maximal removal rate of TDS was 90.6%. When the flowrate was $5\text{m}^3/\text{h}$, the minimal removal rate of TDS was 75.8%; the maximal removal rate of TDS

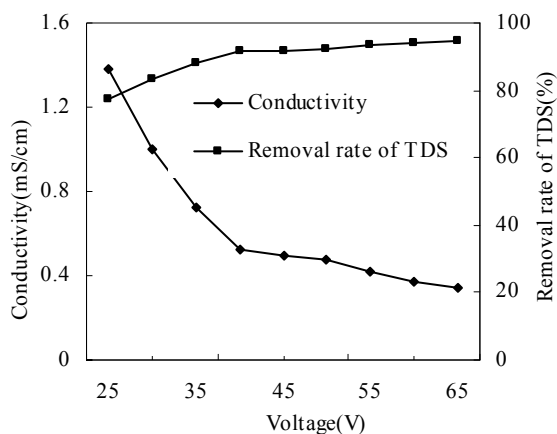


Figure 3(a). Four GS operation effect under $3\text{m}^3/\text{h}$ flowrate.

was 84.3%. According to the test results, it is analyzed that their common operating characteristics are that with the rise of operating voltage, the removal rate of TDS increases, but the treated PFPW conductivity decreases; at the same voltage, with the rise of the flowrate, the removal rate of TDS decreases, the greater the flowrate was, the lower the removal rate of TDS was; at the same removal rate, the greater the flowrate was, the higher the applied voltage was.

Because the set-up pressure can only provide the flowrate of $11\text{m}^3/\text{h}$, in order to determine the maximum treating capacity, the flowrate of the concentrated treated PFPW was reduced, the flowrate of the diluted treated PFPW was increased, and the total flowrate was $11\text{m}^3/\text{h}$. A testing (the flowrate of the concentrated treated PFPW was $4\text{m}^3/\text{h}$, the diluted treated PFPW was $6\text{m}^3/\text{h}$, the rinse solution was $1\text{m}^3/\text{h}$.) was carried out. The results were shown in Figure 4. When the flowrate of the diluted treated PFPW was $6\text{m}^3/\text{h}$, its conductivity can be under $1.3\text{mS}/\text{cm}$ by increasing the voltage, but the energy consumption reached $1.4\text{kW}\cdot\text{h}/\text{m}^3$, which exceeds the design standards. So the maximum treating capacity of the diluted treated PFPW was $5\text{m}^3/\text{h}$.

The lower the flowrate of concentrated treated PFPW, the higher the concentration ratio. Due to that reason, when the concentration difference is much bigger, the selectivity of membranes would be decreased, the reverse osmosis of TDS be increased, which results in the decrease of current efficiency, and the decrease of TDS removal rate. Under the condition of adopting four GS, when the flowrate of the rinse solution was $1\text{m}^3/\text{h}$ and the diluted treated PFPW was $5\text{m}^3/\text{h}$, varying the flowrate of the concentrated treated PFPW, the energy consumption was determined at different ratio of concentrated and diluted treated PFPW.

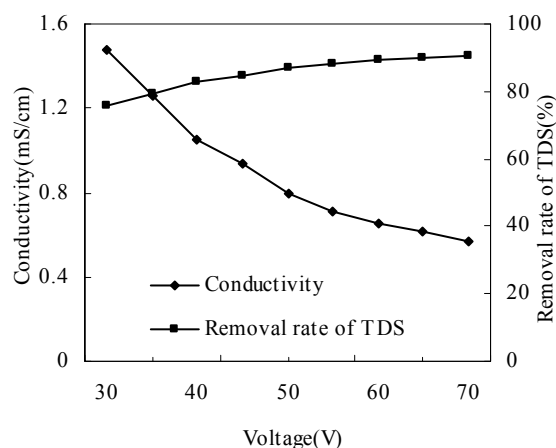


Figure 3(b). Four GS operation effect under $4\text{m}^3/\text{h}$ flowrate.

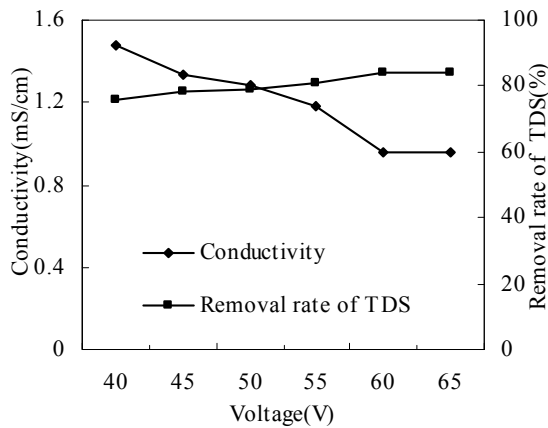


Figure 3(c). Four GS operation effect under 5m³/h flowrate.

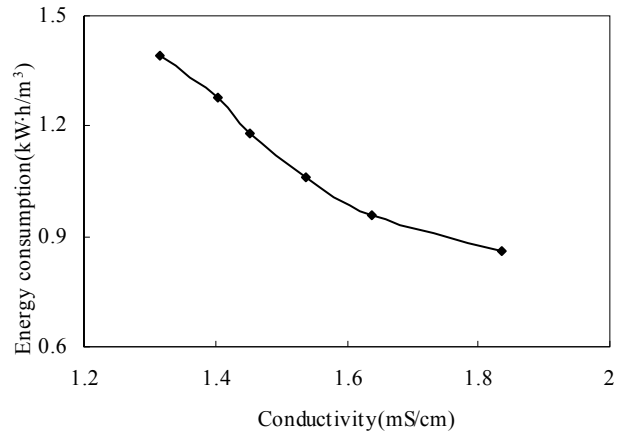


Figure 4. Relation between conductivity and energy consumption.

As shown in Figure 5, when the flowrate of the diluted treated PFPW was 5m³/h, reducing the flowrate of the concentrated treated PFPW, the energy consumption of the same removal rate of TDS were less than 1 kW·h/m³. But the basic trend is that the lower the flowrate of the concentrated treated PFPW, the higher the energy consumption. When the conductivity achieved 1.3mS/cm, which is the stated value, and the flowrate of the diluted treated PFPW was 5m³/h, the energy consumption was the lowest. When the flowrate of the concentrated treated PFPW was 2m³/h, the diluted treated PFPW was 5m³/h and the energy consumption was 0.89kW·h/m³. In order to enhance the production rate and meet the request for energy consumption, the selected flowrate of the concentrated and the diluted treated PFPW was 2m³/h and 5m³/h respectively.

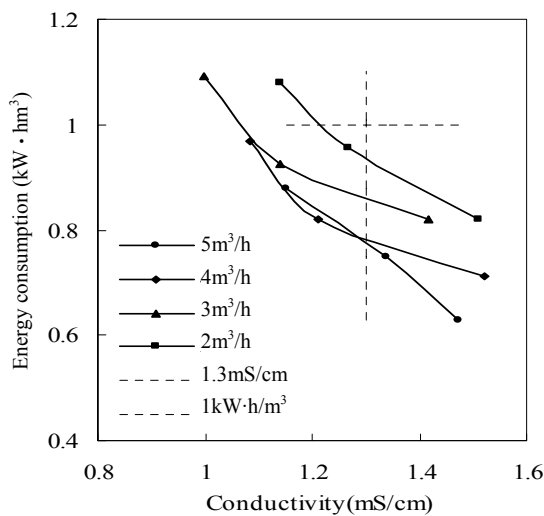


Figure 5. Relation between conductivity and energy consumption at different flowrate of the concentrated treated PFPW.

Under the condition of adopting four GS, the optimal operating conditions are: the flowrate of the rinse solution was 1m³/h, the diluted treated PFPW was 5m³/h, and the concentrated treated PFPW was 2m³/h.

In optimal operating conditions, the treated PFPW has two kinds, one is the diluted treated PFPW whose TDS is less than the original PFPW, the diluted treated PFPW is feasible for confecting polymer solution; another one is the concentrated treated PFPW whose TDS exceeds the original PFPW, the concentrated treated PFPW is feasible for replacing the PFPW as the injecting water in the water-flooding process for high permeability layer. The water quality data about the PFPW, the diluted treated PFPW and the concentrated treated PFPW are presented in Table 1.

The pH values of three types of water are different, as shown in Table 1. The pH of the diluted treated PFPW was lower than the original PFPW, but the pH of the concentrated treated PFPW was higher than the original PFPW. This is because after the original PFPW was treated by the ED set-up, the most HCO₃⁻ that influencing the pH of the original PFPW was concentrated into the concentrated treated PFPW. The HCO₃⁻ of the diluted treated PFPW decreased from 2803 mg/L (in the PFPW) to less than 1000mg/L. So the pH of the diluted treated PFPW was decreased due to the reduction of HCO₃⁻. Finally the pH of the diluted treated PFPW was 7.78, which is alkaline, and it would not lead any corrosion to the preparation and injection equipments and pipelines. Seen from Table 1, the concentrations of some divalent ions such as Ca²⁺, Mg²⁺ are little, so they can not cause scaling when the concentrated treated PFPW was used as the injecting water in the water-flooding process for high permeability layer. It fully meets the pH requirement of confecting polymer solution in oilfields. Therefore, the diluted treated PFPW can be used to confect polymer solution. The pH of the concentrated PFPW is a little higher than the original PFPW. The TDS of the concen-

Table 1. The characteristics of PFPW being used in the test.

	Original PFPW	Diluted treated PFPW	Concentrated treated PFPW
pH	8.50	7.78	8.80
K ⁺ +Na ⁺ (mg/L)	1474.5	245.2	2398.8
Ca ²⁺ (mg/L)	16.0	8.0	44.1
Mg ²⁺ (mg/L)	4.9	2.4	2.4
Cl ⁻ (mg/L)	895.4	97.5	1524.9
SO ₄ ²⁻ (mg/L)	96.1	67.3	38.4
HCO ₃ ⁻ (mg/L)	2135.7	427.2	3417.1
CO ₃ ²⁻ (mg/L)	75.0	0.0	180.1
Polymer (mg/L)	150.3	146.7	151.4
Suspended solids (mg/L)	3.0	2.8	2.9
Oil (mg/L)	2.6	2.7	2.8
TDS (mg/L)	4697.6	847.6	7605.7

trated treated PFPW was about twice of the PFPW. Because there is no specific requirement for the TDS in the injecting water for water flooding in the high permeability layer, the concentrated PFPW with a little higher pH than the PFPW would not bring any effect on water injection production. Therefore the concentrated treated PFPW is feasible to be used to replace the original PFPW as the flooding water in the high permeability layer.

4. Conclusions

This set-up adopts four-grade and four-segment (four GS) electro dialysis reversal technology to desalinate the PFPW. Under the condition of adopting four-grade and four-segment, keeping the ratio of concentrated and diluted treated PFPW flowrate as 1:1, as well as varying the flowrate and voltage, the removal rate under different flowrate was measured. The optimal operating conditions were studied. In optimal operating conditions, the available uses of the diluted treated PFPW and the concentrated treated PFPW were analyzed. Based on the test results, the optimal operating conditions are as follows: the flowrate of the rinse solution was 1m³/h, the diluted treated PFPW was 5m³/h, and the concentrated treated PFPW was 2m³/h. In optimal conditions, the testing results show that the treated PFPW has two kinds, one is the diluted treated PFPW whose TDS is less than the original PFPW, the diluted treated PFPW is feasible for confecting polymer solution; another one is the concentrated treated PFPW whose TDS exceeds the original PFPW, the concentrated treated PFPW is feasible for replacing the original PFPW as the injecting water in the water-flooding process for high permeability layer. This treatment technology can not only decrease environment pollution resulted by the PFPW discharge, but

also achieve closed-circuit of the water resource during crude oil extraction by using polymer flooding technology.

5. References

- [1] D. K. Han, C. Z. Yang, Z. Q. Zhang, Z. H. Lou, and Y. I. Chang, *Journal of Petroleum Science and Engineering*, 22 (1-3), pp. 181-188, 1999.
- [2] D. M. Wang, J. C. Cheng, and J. Z. Wu, *SPE* 49018, pp. 313-317, 1998.
- [3] Q. M. Wang, *Petroleum Geology, and Oilfield Development in Daqing*, 18 (4), pp. 1-5, 1999.
- [4] K. C. Taylor, *SPE* 29008, pp. 675-690, 1995.
- [5] T. L. Chen, Z. Y. Song, Y. Fan, C. Z. Hu, L. Qiu, and J. X. Tang, *SPE Reservoir Evaluation and Engineering*, 1 (1), pp. 24-29, 1998.
- [6] G. L. Jing, X. Y. Wang, and C. J. Han, "The effect of oilfield polymer-flooding wastewater on anion-exchange membrane performance," *Desalination*, 220, pp. 386-393 (Proceedings Greece 2007), 2008.
- [7] R. B. Zhao and X. G. Yue, "Flowing characteristics of 2-acrylamide-2-methyl propane-sulfonic-acid copolymer solution in porous medium," *Journal of Acta Petrolei Sinica*, 26 (2), pp. 85-97, 2005.
- [8] L. Liangxiong, T. M. Whitworth, and R. Lee, "Separation of inorganic solutes from oil-field produced water using a compacted bentonite membrane," *Journal of Membrane Science*, 217, pp. 215-225, 2003.
- [9] G. F. Doran, F. H. Carini, D. A. Fruth, J. A. Drago, and L. Y. C. Leong, "Evaluation of technologies to treat oil field produced water to drinking water or reuse quality," *Proceedings of the Annual SPE Technical Conference*, San Antonio, Texas, 1997.

- [10] J. Pellegrino, C. Gorman, and L. Richards, "A speculative hybrid reverse osmosis electro dialysis unit operation," *Desalination*, 214, pp. 11–30, 2007.
- [11] C. Murray-Gulde, J. E. Heatley, T. Karanfil, J. H. Rodgers Jr., and J. E. Myers, "Performance of a hybrid reverse osmosis-constructed wetland treatment system for brackish oil field produced water," *Water Research*, 37, pp. 705–713, 2003.
- [12] R. Bradley, "Pilot testing high efficiency reverse osmosis on gas well produced water," *Proceedings of the International Water Conference (61st Annual Meeting)*, Pittsburgh, PA, 2000.
- [13] T. Sirivedhin, J. McCue, and L. Dallbauman, "Reclaiming produced water for beneficial use: Salt removal by electro dialysis," *Journal of Membrane Science*, 243, pp. 335–343, 2004.