Study on treatment of acidified waste liquid by process of neutralization/oxidation/flocculation

Xuan Qu¹, Feifei Wang¹, Chengtun Qu¹,²,³ and Tao Yu¹,²

¹College of Chemistry and Chemical Engineering, Xi’an Shiyou University, Xi’an 710065, P. R. China; ²State Key Laboratory of Petrochemical Pollution Control and Treatment, Beijing 102206, P. R. China.
³Email: xianquct@xsyu.edu.cn

Abstract. Acidification technology is an effective measure to increase the production of oil and gas wells and stimulate water injection wells. In order to prevent residual acid from damaging and contaminating the hydrocarbon reservoir, the residual acid should be discharged to the ground for centralized treatment after acidizing process. The present experimental work focused on acidified waste liquid composition analysis of the main pollutants so as to study pH adjustment process and optimization of parameters like dose of hydrogen peroxide and polyacrylamide flocculant. The results show that neutralization-oxidation-flocculation disposal technology enables the treated acidified waste liquid to reach the standard of the combined station sewage treatment system. This study provides theoretical basis and guidance for the process of acidified waste liquid re-injection treatment, the design of sewage treatment and spot application.

1. Introduction

Acidification technology is one of the important measures to improve the production of oil and gas wells and to repair depleted wells [1]. It is used to inject a kind of acid or mixed acids into the formation through the wellbore, which corrode the interconnected pore or natural fissure (hydraulic erosion) on the rock wall in the reservoir, to increase the conductivity of the pores and cracks, and thus achieve the purpose of increasing the production of oil and gas or increasing the injection of water injection wells [2]. The acidic liquid system contains main additives such as hydrochloric acid, hydrofluoric acid, organic acid, corrosion inhibitor, iron stabilizer, bactericide and so on [3,4], contributing to a high amount of pollutants, strong corrosion and high acidity [5]. If acidified waste liquid are discharged directly without treatment, it will cause serious pollution to the surrounding environment [6].

At present, the most frequently used method to treat waste acid is neutralization with lime. When the acidic liquid is neutralized, it can be stored locally or transported to reinject [7]. Due to the complex composition of acidified waste liquid that varied dramatically from each other, the sophisticated treatment process and high costs make the technology still remain in the laboratory stage, which is inconvenient for field application.

To address these issues, based on the analysis of the acidified waste liquids discharged in three different periods from an oil field in Yanan area, this study conducted a series of experimental research which adopted combined process of “neutralization, oxidation, and flocculation”. The work
focused on optimization of parameters and treatment effects of each unit process, so that treated acidified waste liquid can be achieved the standard of entering the sewage treatment system and injected with the waste water for production.

2. Experimental methods

2.1. Apparatus and reagents

Analytical balance (JD200-4), ultraviolet spectrophotometer (UV2350) and constant temperature dryer (202-00AB) are employed.

Sodium hydroxide (NaOH), hydrogen peroxide (H₂O₂) and polyacrylamide (PAM) are all analytically pure. Hydrogen peroxide and polyacrylamide should be prepared when using and do not keep liquid for too long after prepared.

2.2. Measurement

The acidified waste liquids were taken from an oil field in Yanan area during the early, middle, and late stages and were marked as No. 1, No. 2 and No. 3. The experimental tests were performed on three different water samples with the following procedures.

Water quality analysis include: determination of suspended solids by gravimetric method (GB/11901-1989) [8]; according to "Analysis for oil and gas field water" (SY/T5523-2016) [9] and "Recommendation indexes and analysis methods for water quality of clastic reservoirs" (SY/T5329-2012) [10], these methods are suitable for determination of oil content by ultraviolet spectrophotometry, determination of corrosion rate by static coupon test, determination of total hardness by EDTA titration, determination of chloride ion content by silver nitrate titration and determination of divalent iron by iron colorimetric tube.

Neutralization – Oxidation: a beaker was filled with 200mL of acidified waste liquid added NaOH (10%) to adjust the pH; then add different concentrations of H₂O₂ solution for oxidation treatment; after 1h, take the supernatant to detect Fe²⁺ and Fe³⁺ concentration.

Flocculation: a beaker was filled with 200mL of acidified waste liquid after “neutralization-oxidation” treatment and PAM with different concentrations and different molecular weights were added in slant of slow mixture; measure the suspended matter after filtration and separation.

3. Results and discussion

3.1. Analysis of acidified waste water characteristics

Table 1. Water characteristics.

| Parameter                  | No.1   | No.2   | No.3   | Control index |
|----------------------------|--------|--------|--------|---------------|
| pH                         | 0.5    | 5.0    | 5.0    | 7~8           |
| Oil, mg·L⁻¹                | 2.24   | 10.43  | 0.00   | ≤20           |
| Fe³⁺, mg·L⁻¹               | 40.63  | 41.88  | 66.25  | ≤0.3          |
| Fe²⁺, mg·L⁻¹               | 106.25 | 355.00 | 70.00  | ≤0.3          |
| Corrosion rate, mm·a⁻¹     | 0.3110 | 0.0070 | 0.0162 | ≤0.076        |
| SSₐ, mg·L⁻¹                | 23.20  | 184.00 | 39.00  | ≤10           |
| Salinity, mg·L⁻¹           | 62986.20 | 170347.30 | 120675.02 | -           |
| Total hardness, mg·L⁻¹     | 5170.41 | 49134.53 | 31167.63 | -            |

ₐ SS, suspended substances.

The experimental tests were performed on three different water samples (Table 1). Sample No. 1 was milky white, samples No. 2 and No. 3 were dark brown with pungent odor. A large amount of foam was generated during stirring. Table 1 shows that the acidity of the waste liquid is the strongest during
the early stage of returning, and the three kinds of acidified waste liquids all have the features of high suspended solid content, strong corrosion, and high total iron, indicating that the main indexes are much higher than the water quality requirements of the oilfield's reinjection water according to "Recommendation indexes and analysis methods for water quality of clastic reservoirs" (SY/T5329-2012) [10].

In terms of the characteristics of acidified waste water quality and the entry requirements of the sewage treatment system, unit treatment process was studied and various process parameters were optimized.

3.2. Study on neutralization, oxidation and flocculation treatment of Acidified Waste Liquid in laboratory

3.2.1. Neutralization - Oxidation. No. 1 acidified waste liquid: The experiment shows that the pH is adjusted to 3-4, adding H2O2 of different concentrations range from 0.4% to 0.7%, divalent iron is all oxidized to trivalent iron. While the dose of H2O2 is more than 0.8%, some of the divalent iron is not oxidized. The results were shown in Table 2. According to the reaction mechanism of Fenton reagent, Fe2+ plays an important role in catalyzing the decomposition of H2O2 to generate hydroxyl radicals, and Fe3+ produced in the catalytic process is transformed to Fe2+, which is recycled so that the reaction can continue [11]. The essence of Fenton reagent is the chain reaction between Fe2+ and H2O2, catalyzing the generation of hydroxyl radicals. Jeseph maintained the Fenton reagent’s reaction process is as follows [12, 13]:

$$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \cdot \text{OH} + \text{Fe}^{3+} + \text{OH}^- \quad (1)$$

$$\text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (2)$$

If the concentration of H2O2 is too high in Fenton system, excess hydrogen peroxide will inhibit the conversion of divalent iron to trivalent iron. Because the reaction rate is so slow that produce few hydroxyl radicals, the whole process is limited.

In addition, in this set of experiments, it was perceived that the pH was adjusted to 3-4, and the total iron content was still high after hydrogen peroxide oxidation. Therefore, after several tests, it was found that adjusted pH to 10, the water supernatant became clearer and brighter. The reason is that as the pH increasing, trivalent iron salts form a series of multinuclear complexes in the water, which can exert a good electric neutralization effect, making colloids and suspended solids reach isoelectric state and destabilize or precipitating particles [14]. Overall, trivalent iron salts can play the role of purified water.

| Oxidant dosage | 0.4% | 0.5% | 0.6% | 0.7% | 0.8% | 0.9% |
|---------------|------|------|------|------|------|------|
| Fe3+, mg·L⁻¹  | 178.75 | 147.50 | 137.50 | 102.50 | 153.75 | 150.00 |
| Fe2+, mg·L⁻¹  | 0.00 | 0.00 | 0.00 | 0.00 | 6.25 | 18.75 |

So the following experiments were carried out, the pH was determined to 10.

| Oxidant dosage | 0.05% | 0.1% | 0.2% | 0.3% | 0.4% | 0.5% | 0.6% |
|---------------|------|------|------|------|------|------|------|
| Fe3+, mg·L⁻¹  | 0.00 | 0.04 | 0.14 | 0.31 | 0.45 | 0.51 | 0.36 |
| Fe2+, mg·L⁻¹  | 0.13 | 0.04 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 |

Results in Table 3 imply that the content of trivalent iron gradually increased and then decreased with the growing of hydrogen peroxide dosage, and the divalent iron was basically converted to trivalent iron. Therefore, the optimized dosage of hydrogen peroxide is 0.2% at pH of 10.
No. 2 acidified waste liquid:

Table 4. Ferrous and ferric iron concentrations of No.2 sample.

| Oxidant dosage | 0.2% | 0.3% | 0.4% | 0.5% |
|----------------|------|------|------|------|
| Fe$^{3+}$, mg·L$^{-1}$ | 0.00 | 0.00 | 0.02 | 0.02 |
| Fe$^{2+}$, mg·L$^{-1}$ | 0.23 | 0.18 | 0.13 | 0.13 |

Results in Table 4 show that the pH adjusted pH to 7.4-7.5, the divalent iron was basically converted to trivalent iron with increasing amount of hydrogen peroxide added. Although the content of Fe$^{3+}$ reduced to zero with the hydrogen peroxide dosage range from 0.2% to 0.3%, content of Fe$^{2+}$ is not the lowest value at this time. In addition, Fe$^{2+}$ content is the lowest after adding 0.4% hydrogen peroxide and Fe$^{3+}$ content is only 0.02 mg/L. With the increase of the amount of hydrogen peroxide, the color will be deeper and darker, which will affect the removal of color and the subsequent flocculation process effect. Taking into account the cost factor, the hydrogen peroxide dosage is determined to be 0.4% at pH of 7.4-7.5.

No. 3 acidified waste liquid:

Table 5. Ferrous and ferric iron concentrations of No.3 sample.

| Oxidant dosage | 0.05% | 0.06% | 0.1% | 0.2% | 0.3% |
|----------------|------|------|------|------|------|
| Fe$^{3+}$, mg·L$^{-1}$ | 0.00 | 0.23 | 0.00 | 0.00 | 0.60 |
| Fe$^{2+}$, mg·L$^{-1}$ | 0.03 | 0.09 | 0.18 | 0.20 | 0.69 |

Results in Table 5 show that the pH adjusted pH to 7.4-7.5, the divalent iron was basically converted to trivalent iron. Consequently, the optimized dosage of hydrogen peroxide is 0.05% at pH of 7.4-7.5.

3.2.2. Flocculation. Flocculation is one of the most common methods for treating acidified waste liquid from oil fields. It is often used to add agents to remove insoluble and some soluble substances in the waste liquid through the "flocculation - precipitation" process.

Due to the high content of iron in the acidified waste water, in the neutralization-oxidation stage, the polymer converted from the trivalent iron salts in the waste liquid has coagulated some of the organic matter and suspended matter. At this time, flocculant is only demanded to be added to improve the coagulation effect. Considering the wide range of performance and application, this experiment employed polyacrylamide as flocculant for the treatment of acidified waste liquid [15]. The result is shown in Figure 1.

The experimental results show that the addition of PAM can effectively enhance the coagulation effect and the removal rate of suspended substances and oil is increased. When the dose of PAM was insufficient, the removal rate of suspended solids was relatively low. With the increase of PAM dosage, the removal rate of suspended solids increased. In this experiment, the optimized concentration of PAM for No. 1 and No. 3 samples is determined to be 5 mg·L$^{-1}$, and the optimized concentration of PAM for No. 2 sample is 3 mg·L$^{-1}$. As the water samples undergo neutralization-oxidation, the divalent iron is basically converted to trivalent iron. At this time, the No.2 water has the highest trivalent iron content and can be converted into more polymers. Therefore, only a small amount of PAM which is less than No.1 or No.3 sample can achieve the effect of removing suspended solids.
3.3. Composite processing effect

The characteristics of the treated acidified waste liquid are shown in the Table 6. Through combined process of “neutralization, oxidation, and flocculation”, acidified waste liquids such as trivalent iron, divalent iron, suspended solids, etc., are reached to entering of the sewage treatment system.

| Parameter | No.1 | No.2 | No.3 |
|-----------|------|------|------|
| pH        | 7.0  | 7.0  | 7.0  |
| Fe$^{3+}$,mg·L$^{-1}$ | 0.01 | 0.00 | 0.00 |
| Fe$^{2+}$,mg·L$^{-1}$ | 0.14 | 0.10 | 0.21 |
| SS,mg·L$^{-1}$ | 0.00 | 30.00 | 0.00 |

4. Conclusions

Changing the pH of acidified waste liquids not only make the trivalent iron salt convert into polymer to coagulate part of the organic matter and suspended matter in water, but also achieve reducing the total iron content. The optimum dosage of hydrogen peroxide is selected with the content of divalent iron and trivalent iron as indicators, and the optimized dosage of No. 1, No. 2 and No. 3 water is 0.2%, 0.4%, 0.05% respectively. In addition, the optimum concentration of PAM for No. 1 and No. 3 samples is 5 mg·L$^{-1}$ with the removal rate of suspended substances as the index. The optimum concentration of PAM for sample No. 2 is 3 mg·L$^{-1}$.

The acidified waste liquid treated by the "neutralization-oxidation-coagulation" composite process achieves the criteria for entering the sewage treatment system of the combined station, and has good compatibility with the sewage and low corrosiveness, and can follow the sewage reinjected together for production.

Acknowledgement

This research was financially supported by National Science and Technology Major Project of China. (No. 2016ZX05040-003)
References

[1] Ma Yun, He Shun'an, Hou Yalong 2009 Research progress of the damage of waste fracturing fluids in oil fields and treatment technology J. Petrochemical Industry Applications 28(8) 1

[2] Chen Dajun 2006 M. Oilfield Applied Chemistry Petroleum Industry Press

[3] Liu D, Fan M, Yao L, et al 2010 A new fracturing fluid with combination of single phase microemulsion and gelable polymer system J. Journal of Petroleum Science & Engineering 73(3) 267

[4] Aminto A, Olson M S 2012 Four-compartment partition model of hazardous components in hydraulic fracturing fluid additives J. Journal of Natural Gas Science & Engineering 7(3) 16

[5] Fan Qingyu, He Huanjie, Wang Yonghong, et al 2002 Research Progress of Drilling Wastewater and Acidification Fracturing Operation Wastewater Treatment Technology J. Oil Field Chemistry 19(4) 387

[6] Ding Zhen, Du Chun'an, Yuan Changzhong 2016 Neutralization-oxidation-coagulation combined treatment of acidified waste liquid in oil fields Chinese J. Journal of Environmental Engineering 10(8) 4319

[7] Wei Xiufen 2007 Discussion on Treatment Technology of Fracturing Acidification Treatment Backflow Liquid J. Oil Field Chemistry 24(4) 384

[8] GB 11901-1989 Water quality-Determination of suspended substance-Gravimetric method China Standard Press 1989 192

[9] SY/T 5523-2016 Practice for analysis of oilfield waters Petroleum Industry Press 2016

[10] SY/T 5329-2012 Water quality standard and practice for analysis of oilfield injecting waters in clastic reservoirs Petroleum Industry Press 2012

[11] Su Rongjun 2008 Study on the Effect of Fenton Reagent on Oxidation of Wastewater and Inorganic Ions J. Journal of Harbin University of Commerce (Natural Science Edition) 24(2) 210

[12] Xiong Zhong, Lin Yan 2002 Application of Fenton Oxidation in Wastewater Treatment J. Environmental Protection of Xinjiang 24(2) 35

[13] Zhang Yufen, Sun Jian 2006 Study on Oxidation and Viscosity Reduction of Fractured Waste Liquid by Fenton Reagent J. Oil & Gas Chemical Industry 35(6) 493

[14] Wen Yanjie 2012 Preparation and properties of polysilicate ferric magnesium coagulant D. Beijing University of Chemical Technology

[15] Tang Shouyin, Dai Youzhi, Wang Dayi 2004 Wastewater Treatment Engineering M. (Second Edition) Chemical Industry Press