CSCanada
Advances in Petroleum Exploration and Development
Vol. 19, No.2, 2020, pp. 83-88
DOI:10.3968/12022

ISSN 1925-542X [Print]
ISSN 1925-5438 [Online]
www.cscanada.net
www.cscanada.org

Experimental Study on Desilication of Heavy Oil Wastewater in Shengli Oilfield

LI Jinzhi[a]; GUAN Lei[b]; XU Yunxian[b]; YU Dandan[c]; PAN Yongqiang[c],*

[a]Oil and gas development management center of Shengli Oilfield Company, China.
[b]Dongxin oil production plant of Shengli Oilfield Company, China.
[c]Petroleum Engineering Technology Research Institute of Shengli Oilfield Company, China.
*Corresponding author.

Received 20 September 2020; accepted 3 December 2020
Published online 31 December 2020

Abstract
The scaling problem of silicon in the heavy oil production of Shengli Oilfield will seriously affect the normal production and production. According to SYT 5523-2006 oilfield water analysis method, the ions in the water samples collected by each water treatment unit were analyzed, and it was found that the content of metasilicic acid in the high-temperature separation water was relatively high, so the effect of four kinds of desilication agents was studied in this paper. It is found that the effect of desilication agent is the best. Magnesium agent is selected as desilication agent. Through the orthogonal experiment of three factors designed by SPSS software, the factors influencing desilication effect are investigated. Through the analysis of SPSS, it is found that the effect of temperature on the experimental results is not significant. After comprehensive investigation, it is concluded that the effect of desilication is the best when the dosage of agent is 400mg/L, and the effect of desilication is the best when the pH is 10. According to the experimental data, it can be seen that the effect of desilication is the best when the dosage is 400mg/L The removal rate of silicon can reach more than 90%.

Key words: Heavy oil sewage; Silica scale; SPSS; Dosage; Removal rate

Li, J. Z., Guan, L., Xu, Y. X., Yu, D. D., & Pan, Y. Q. (2020). Experimental Study on Desilication of Heavy Oil Wastewater in Shengli Oilfield. *Advances in Petroleum Exploration and Development*, *19*(2), 83-88. Available from: http://www.cscanada.net/index.php/aped/article/view/12022
DOI: http://dx.doi.org/10.3968/12022

Preface: The steam flooding technology adopted in Shengli Oilfield will produce a kind of high-temperature separated water with high salinity and silicon content. The ions in the high-temperature separated water will accumulate continuously in the circulation process, which will have a serious impact on the sewage treatment unit, pipelines and boilers, resulting in frequent scaling of boiler pipes. Through the analysis of the collected scale sample, it is found that the scale sample is silicon scale. In addition, conventional descaling methods, such as pickling, are difficult to remove, which will eventually lead to perforation or even scrap of furnace tubes and steam injection pipelines. In the whole sewage treatment system, the original desilication system does not operate continuously and effectively, resulting in a large number of silicon ions in the treated water. Through the analysis of water samples, it is also confirmed that the content of silicon ions in the water is too high. There are some problems in the original process, and there are some disadvantages in the desilication agent. Therefore, it is of great significance to select the appropriate desilication agent or desilication formula for desilication and antiscaling of heavy oil wastewater.

1. EXPERIMENTAL MATERIALS AND METHODS

1.1 Materials

See Table 1 for materials and instruments used in the experiment. In the experiment, the water samples of the treatment unit were collected and analyzed according to the oilfield water analysis method (Syt 5523-2006). The total alkalinity, bicarbonate, carbonate and hydroxide were titrated by Potentiometric method, with glass electrode as indicator electrode, calomel electrode as reference electrode, and acid standard solution as titration, and the end point was indicated by pH meter. The content of metasilicic acid in the water sample is determined by silicon molybdenum yellow spectrophotometry. In the acid solution, the reaction between soluble silicic acid and ammonium molybdate can generate yellow silicon molybdenum heteropoly acid. Within the concentration range, the content of metasilicic acid in the water sample is determined according to the proportion between the absorbance and the content of soluble silicic acid [1].

Table 1
Details of main materials and instruments

Material and Instrument	Manufacturer	Purity
Hydrochloric acid	Laiyang Chemical Reagent Factory	Analytical purity
Ammonium molybdate	Laiyang Chemical Reagent Factory	Analytical purity
Oxalate	Laiyang Chemical Reagent Factory	Analytical purity
Sodium hydroxide	Laiyang Chemical Reagent Factory	Analytical purity

1.2 Screening of Desilication Agents

For the wastewater containing silicon, different types of desilication agents have certain effect. The commonly used desilication and coagulation agents are magnesium agent, aluminum agent and iron agent [2]. In this experiment, different desilication agents were selected to carry out desilication experiments on simulated water samples, and the most ideal desilication agent was selected. Then, the single factor tests of the dosage, reaction temperature and reaction pH value of the target desilication agent were carried out to determine the best reaction conditions of the target agent.

The initial concentration of metasilicic acid in the simulated water sample is 400 mg/L, and the desilication performance of four agents, magnesium agent, calcium salt, aluminum salt and iron salt, is investigated. According to the temperature and pH of the high-temperature separated water, the reaction pH value is set as 10.0, the reaction temperature is set as 90 ℃, and the test is carried out under the conditions of the dosage of agent is 100 mg/L and the reaction time is 20 min.

1.3 Analysis of Factors Affecting the Effect of Desilication Agent

Take 100 ml of simulated water sample and heat it in a constant temperature water bath to the reaction temperature. Keep the temperature constant during the reaction. Adjust the pH value with 20% NaOH and hydrochloric acid 1+1. During the reaction, adjust the pH value at any time along with the dosing of the agent to keep the solution within the range of the set pH±0.5. When the pH = 8, 9, 10, 11 and 12, select 60℃, 70℃, 80℃, 90℃ for the reaction temperature, and 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L and 500 mg/L for the dosing of magnesium agent mg/L slowly add the target agent and stir at the same time. When adding the medicine, stir quickly for 1 minute at a speed of 200 rpm, and then continue to react for 19 minutes at a speed of 50 rpm. After the reaction, filter with medium speed filter paper and detect the content of metasilicic acid in the filtrate.

2. EXPERIMENTAL RESULTS AND DISCUSSION

2.1 Water Quality Analysis Results

After treatment, the hardness of water has been improved, the content of Ca^{2+} and Mg^{2+} is basically 0, but the anion has not been effectively removed, and the content of metasilicic acid is very large, which is the most critical ion to cause scaling.

Table 2
Analysis results of water quality index of heavy oil sewage

Sample number	Total alkalinity（CaCO3）	pH	HardnessCaCO3，mg/L	Ca，mg/L	Mg，mg/L	H2SiO3，mg/L
Floatation effluent	671.67	7.5	76.4	29.93	0.378	55.291
Desilication effluent	668.37	8.4	75.1	22.78	4.36	48.805
Softened effluent	640.84	8.2	2.0	0	0.48	52.492
External water conveyance	1046.05	10	12.5	0	3	78.577
High temperature separated water	3049	11.4	2.2	0	0.528	411.086

2.2 Drug Screening Results

The concentration of the four solutions is 100 mg/L, which is based on the actual concentration of ions (Mg^{2+}, Ca^{2+}, Al^{3+}, Fe^{2+}). Use the reagent name as the abscissa and the removal rate of metasilicic acid as the ordinate, as shown in Figure 1.

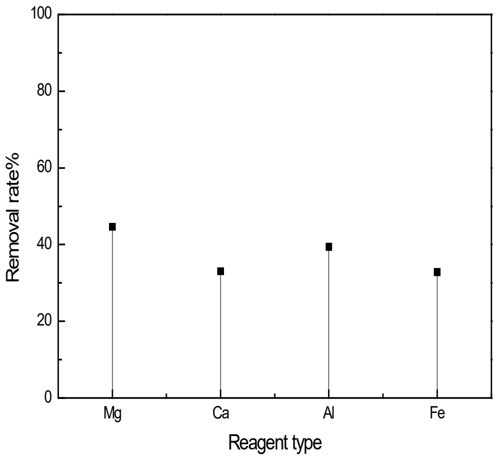

Figure 1
Comparison of desiliconization effect of different types of drugs

It is found that the effect of single agent is not significant, and the silicon removal rate of four agents is not more than 50%. Among them, the silicon removal rate of 100 mg/L magnesium compound is 44.66%. $Mg(OH)_2$ is generated after dissolving in water, which can react with metasilicic acid in water quickly, and the silicon removal effect is the best. The removal rate of aluminum agent is 39.45%, slightly lower than that of magnesium agent, and the effect of calcium agent and iron agent are poor, which are 33.07% and 32.81% respectively. In the experiment, it is found that magnesium and calcium are colorless and transparent when they are made into 100 mg/L solution, aluminum is slightly sticky when they are dissolved in water, and iron is yellowish brown when they are dissolved in water. Magnesium agent and aluminum agent will hydrolyze rapidly after dissolving in water. The main components in the agent react with metasilicic acid in water rapidly to form white floccules. The supernatant will be clear after precipitation, while the floccules formed in the reaction process of calcium agent are less. Magnesium agent can remove silica by forming magnesium silicate precipitate in alkaline condition [3]. At the same time, as a water treatment agent, magnesium salt has the advantages of fast floc formation, large and dense particles, fast floc settling speed, good turbidity removal and decolorization effect[4], and Mg^{2+} is non-toxic and easy to be separated from sludge . According to the desilication effect of four agents, magnesium agent was selected as the following desilication agent.

2.3 Influencing Factors Analysis Experiment

The orthogonal experiment was designed with SPSS software, and 25 groups of experiments were designed in total. After the reaction under the set conditions, the supernatant was taken and the content of metasilicic acid was measured by silicon molybdenum yellow spectrophotometry. The analysis results are as follows.

Table 3
Test of intersubjective effects (dependent variable: silicon removal rate)

Source	Class III sum of squares	Df	Mean square	F	Saliency
Calibration model	6256.124a	11	568.739	9.095	0.000
Intercept	80956.724	1	80956.724	1294.676	0.000
Temperature	206.058	3	68.686	1.098	0.384825
Dosage	1602.514	4	400.628	6.407	0.004478
pH	4447.552	4	1111.888	17.782	0.000034
Error	82.896	13	62.530		
Total	98091.910	25			
Total corrected	7069.020	24			

It can be seen from Table 3 that the significance of dosage and pH is 0.004 and 0.000 respectively, which are less than 0.005, so the dosage and pH have obvious effect on the dependent variable silicon removal rate, while the significance of temperature is 0.385, indicating that the temperature has little effect on the dependent variable. Therefore, the dosage and pH were further analyzed.

Table 4
Multiple comparisons (dependent variable: silicon removal rate)

Dosage	Comparison of dosage	Saliency	pH	Compare pH	Saliency
100	200	0.021	8	9	0.001
	300	0.004		10	0.000
	400	0.001		11	0.000
	500	0.001		12	0.000
200	100	0.021	9	8	0.001
	300	0.389		10	0.010
	400	0.159		11	0.020
	500	0.084		12	0.064
300	100	0.004	10	8	0.000
	200	0.389		9	0.010
	400	0.556		11	0.717
	500	0.345		12	0.338
400	100	0.001	11	8	0.000
	200	0.159		9	0.020
	300	0.556		10	0.717
	500	0.713		12	0.543
500	100	0.001	12	8	0.000
	200	0.084		9	0.064
	300	0.345		10	0.338
	400	0.713		11	0.543

According to the comparison results of two levels in Table 4, when the dosage is 100 mg/L, the difference between the dosage and other four groups is less than 0.05, indicating that there is significant difference between the dosage at 100 mg/L and other doses, which is consistent with the comparison data at other doses. When the dosage is increased to more than 100 mg/L, the treatment effect is enhanced, and the change of experimental results is obvious. However, when the dosage is more than 100 mg/L, it is more than 0.05 compared with other dosages, which shows that the effect changes steadily after the dosage is more than 100 mg/L, but the difference is not significant.

The multiple comparison results of pH value show that when pH value is less than 9, the significant difference between pH value and other pH values is less than 0.05, indicating that pH value at 8 and 9 has little effect on the desilication effect, which may be due to the fact that magnesium agent is not easy to form hydroxide when alkalinity is small, thus affecting the reaction between desilication agent and metasilicic acid in water. When the pH is greater than 9, the experimental results change obviously, and the treatment effect is enhanced. When the pH is more than 10, the significance is greater than 0.05, and the effect of pH on the data is stable.

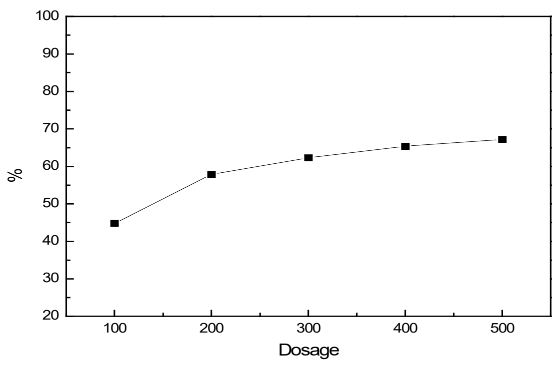

Figure 2
Effect of dosage of chemicals on treatment effect

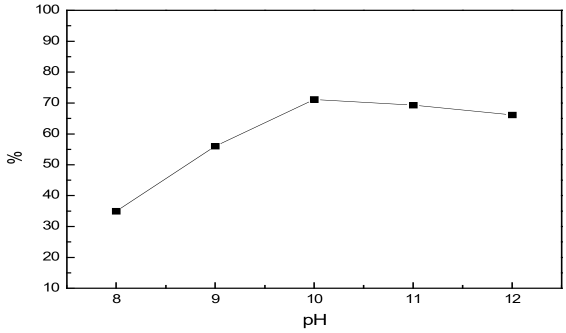

Figure 3
Effect of reaction pH on treatment effect

As shown in Figure 2, with the increase of dosage, the efficiency of silicon removal is also increasing, showing a positive correlation trend. When the dosage is 500 mg/L, the maximum removal rate is 67.224%; when the dosage is increased from 100 mg/L to 200 mg/L, the maximum removal rate is 29.17%. When the dosage is more than 200 mg/L, the removal rate of metasilicic acid is steadily increased, and the removal rate of silicon is significantly improved. The reason is analyzed: the increase of AM dosage, the increase of floccule surface area formed after dissolution of traditional Chinese medicine solution, and the significant increase of the interaction area with the charged negative silicate ion in the solution. The deposition of agent and silicate ion in the electric neutralization and bridging net catching is reflected in the significant increase of total silicon removal rate [5]. However, when the dosage is too much, due to the hydrolysis effect, the pH of the solution will be reduced [6], and the low pH can not adapt to the subsequent processing unit. At this time, in order to adjust the pH of the solution, the cost will be increased. In a comprehensive consideration, the dosage of 400 mg/L is the best.

It can be seen from Figure 3 that the reaction pH has a significant impact on the desilication effect. When the pH is 8-10, the removal rate shows an increasing trend with the increase of the reaction pH. when the pH=10, the removal rate reaches the highest level, and when the pH continues to rise, the removal rate shows a downward trend. The overall trend is a broken line. The average removal rate of silicon was 34.956% at pH 6, increased to 56.05% at pH 9, and decreased to 69.28% at pH 11. The reason is that silicic acid in water mainly exists in four different forms: soluble silicic acid (H_4SiO_4), polysilicate $[(SiO_2)_m(H_2O)_n]$, silicic colloid (polysilicate with a diameter of >5nm) and silica (with a diameter of > 0.45mm)[7]. At pH 8 ~ 9, the silicon in the water sample mainly exists in the form of orthosilicic acid h4sio4, which is weak acid. When the desilication agent is added, the desilication mechanism of the agent is mainly coagulation; when the pH rises to 10, more hydrogen peroxide in the solution will promote the dissociation of the silicic acid part to form $H_3SiO_4^{2-}$ and $H_2SiO_4^{2-}$, and the solution presents weak electronegativity. The dissolution of magnesium agent in water will form floccules, which are weakly positively charged. Due to the action of neutralization and adsorption, the dissociated $H_3SiO_4^{2-}$ and $H_2SiO_4^{2-}$ will react with the floccules rapidly and form precipitates. When the number of flocs increases, the removal rate of silicon will also be improved by bridging net catching; however, when the alkalinity of solution is too high, most of silicic acid dissociates to form $H_2SiO_4^{2-}$, resulting in electrical exclusion, and the hydrolysis of desilication agent is also inhibited, resulting in the weakening of the neutralization and adsorption of desilication agent, so the removal rate will not increase but decrease.

From the above analysis, it is found that 400 mg/L is the best for the dosage of the agent; for pH, the effect of desilication is the best when pH=10, and the temperature factor has no significant influence in the experiment, so it can be selected at will. In order to reduce the cost of desilication, the temperature of desilication is the temperature of high-temperature separated water.

3. CONCLUSION

(1) According to the types of commonly used desiliconizing agents, four desiliconizing agents with different components are selected, and their desiliconizing effects are systematically investigated. Finally, through the agent screening test, the results show that the desiliconizing efficiency of the magnesium agent selected in this paper is the highest; the desiliconizing rate is 44.66%, which is better than that of the aluminum, calcium and iron agents. In the test, magnesium agent is selected as desiliconizing agent, and the influencing factors of desiliconizing effect are studied.

(2) Through SPSS design orthogonal experiment, and through the software analysis of significance, it is found that the dosage and pH have the greatest impact on the experimental results. Through the comparison between the two, it is

found that the treatment effect is gradually obvious when the dosage of the agent is greater than 100 mg/L, and the pH changes significantly when it is greater than 9. Finally, according to the analysis of the average figure, the dosage of the magnesium agent is 500 mg/L when the desilication rate is the largest. However, considering the cost of maintaining the pH of the water sample, the comprehensive operation cost and other factors, the optimal dosage of the magnesium agent is 400 mg/L, the reaction pH is 10.0, and the reaction temperature is determined It has little effect on the experimental results, because the temperature of high-temperature separation water treatment is about 80℃, so 80℃ is selected to avoid other consumption of temperature rise and temperature drop, and the removal rate can reach the best effect.

REFERENCES

[1] State health and Family Planning Commission of the people's Republic of China, State Food and drug administration (2016). Gb8538-2016. *National food safety standard for drinking natural mineral water inspection method*. Beijing: China Standards Press.

[2] Du, C., Arjuna, B. C., et al (2017). Research progress of silicic acid scale and its control method. *Industrial Water Treatment, 37*(10), 6-10.

[3] Zhao, Z. X., Han, G. H., Li, R. L., et al (2004). Study on chemical desilication technology of heavy oil wastewater recycling boiler. *Industrial Water Treatment, 24*(8), 28-30.

[4] Liu, X. C., Zhang, Y., Zhou, Q., et al (2009). Characterization and application of magnesium iron composite flocculant. *China Environmental Science, 29*(6), 646-650.

[5] Geng, Q. X. (2014). *Research on silicon scale control technology of thermal recovery boiler for heavy oil wastewater reuse*. China University of mining and technology.

[6] Qiu, Z., Huang, X. F., Wen, Y., et al (2005). Experimental study on desilication of thermal recovery boiler for heavy oil wastewater reuse. *Environmental Engineering, 13*(4), 83-88.

[7] Sanciolo, P., Milne, N., Taylor, K., et al (2014). Silica scale mitigation for high recovery reverse osmosis of groundwater for a mining process. *Desalination, 340*(1), 49-58.

