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Characteristic analysis and evaluation of chlorine dioxide mixed with oilfield sewage

Baojuan Ye

No.9 Oil production plant, Daqing Oilfield Ltd., Daqing, China

Abstract. In order to ensure the bactericidal quality of oilfield reinjected sewage and improve the utilization ratio of oilfield sewage reinjected, the experiment of chlorine dioxide mixed with oilfield sewage was carried out. Two oxygen chlorine disinfectant mixed water flooding was used to produce sewage and polymer flooding sewage, and the characteristics of mixing were analyzed. Ultraviolet radiation, conventional or high concentration bactericides are not durable, the bacterial quantity of injected wellhead is obviously restored, and the field applicability is poor; negative pressure chlorine dioxide bactericidal technology is better than positive pressure method, and its sulfate reducing bacteria (SRB), saprophytic bacteria (TGB) and iron bacteria (IB) kill nearly 100%, the cost is the lowest, and the high efficiency is maintained. For a long time, chlorine dioxide is used to sterilize polymer flooding wastewater to clean up dilute or dirty polymer. The solution has high initial viscosity, low viscosity loss and high viscosity retention rate. This study provides technical support for the two utilization of oilfield water drive and polymer flooding wastewater.

Key words: Chlorine dioxide; sewage; sterilization; viscosity

1. Introduction

Chlorine dioxide is a strong oxidant. Besides disinfecting and sterilizing, it also has many properties such as anti-corrosion, anti-mold, fresh-keeping, deodorizing and bleaching. It is widely used and is a commonly used disinfectant [1-3]. In the case of disinfectant, it is often insensitive to temperature, and the sterilizing ability is basically unchanged in cold and hot state; it is not sensitive to pH, and can be efficiently sterilized at pH between 2 and 10 [4-5]. The dosage is small, the concentration is only half of the chlorine gas, and the same sterilization effect can be achieved.

2. Chlorine dioxide mixed with water-driven sewage

2.1. Sewage sampling

Water was taken from the joint stations A to F, and the amounts of (SRB), (TGB) and (IB) were measured, as shown in Table 1.



Table 1. Determination of bacteria in water samples

Source of water sample	Sulfate reducing bacteria (/ml)	Saprophytic bacteria (/ml)	Iron bacteria (/ml)
A Joint station	6.0×10^4	6.0×10^3	2.5×10^4
B Joint station	2.5×10^4	1.1×10^4	2.5×10^4
B Joint station	2.5×10^3	2.5×10^4	6.0×10^4
D Joint station	6.0×10^4	2.5×10^4	1.3×10^3
E Joint station	1.1×10^4	1.1×10^4	1.1×10^4
F Joint station	6.0×10^4	2.5×10^4	6.0×10^4

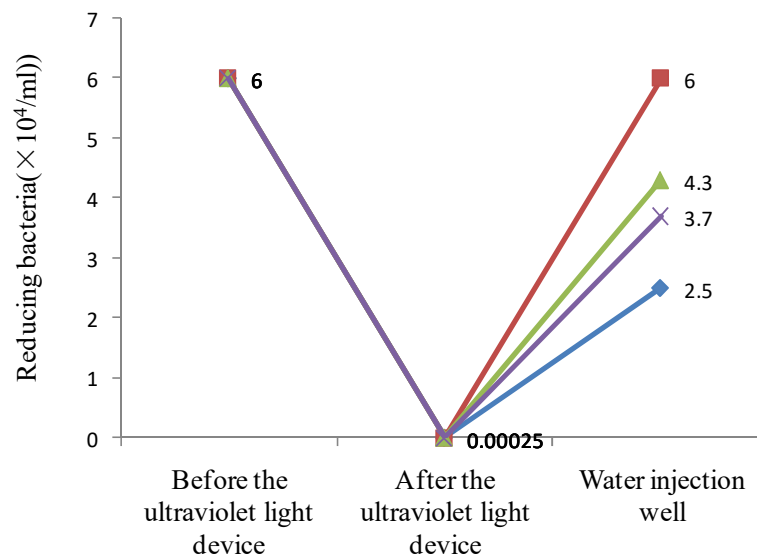
In the sample, the number of bacteria contained in the unit water was 104 orders of magnitude. Among them, the sample containing the F station has the largest number of three kinds of bacteria, so the water sample is used as the experimental liquid.

2.2. Experimental comparison

The combined water treatment station sterilization technology is often sterilized by ultraviolet rays, conventional fungicides and high-concentration fungicides. The effects of common sterilization techniques were collected and compared with chlorine dioxide.

(1) Ultraviolet bactericidal efficacy

The experiment uses an ultraviolet disinfection device of the F joint station installed on the inlet pipe of the water injection pump, and the treatment capacity is 5000 cubic meters per day. The experimental results are shown in Fig. 1. After the sewage is passed through the device, the number of SRBs is significantly reduced. However, by measuring the number of SRBs in the four injection wells, it was found that the number of the SRBs rebounded significantly, which indicates that the ultraviolet sterilization is effective in a short time, but the sterilization effect cannot be sustained in the sewage transportation process.

**Fig 1.** Bactericidal effect diagram of ultraviolet radiation

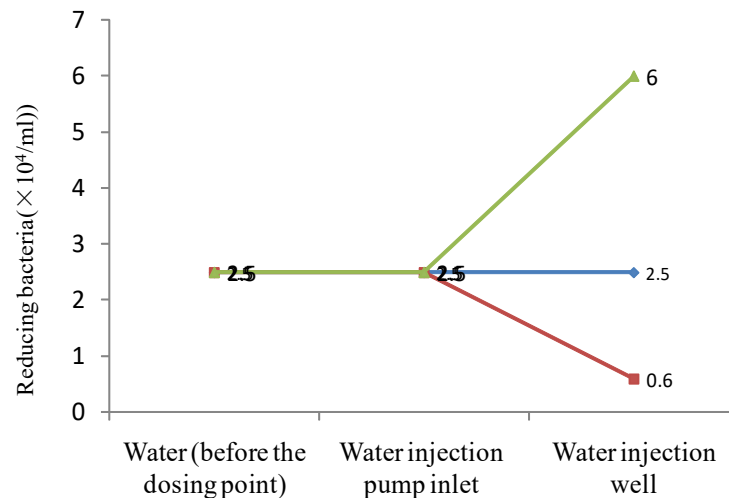


Fig 2. Germicidal efficacy of 50mg/L at dosing concentration

(2) Sterilization test using conventional water-flooding fungicide

In the inlet of the filter tank, Daqing refining LDS-1 type medicaments of three levels of 50 mg/L to 200 mg/L were used for sterilization. The SRB content of the 8-day water injection wellhead was measured, as shown in Figures 1 to 2.

(3) Chlorine dioxide sterilization test

Chlorine dioxide is usually produced by two methods, a positive pressure method and a negative pressure method. The two methods of positive pressure method and negative pressure method were respectively used to generate chlorine dioxide, and then mixed with sewage. The dosing point is selected on the inlet pipe of the injection pump (positive pressure method, negative pressure method) or before the water injection buffer tank (negative pressure method). Figure 6

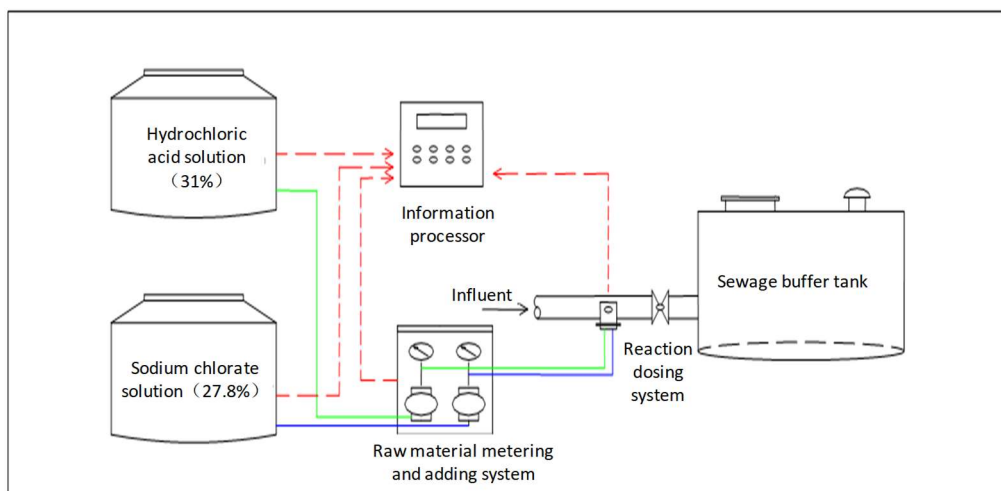


Fig 3. Schematic diagram of chlorine dioxide negative pressure sterilization device

The injection water SRB data is collected by setting a sampling point at each of the water injection tank outlet before sterilization, the inlet of the water injection pump after sterilization, and the three single wells downstream of the water injection station. Wells A, B and C are less than 4 km from the water injection station.

Positive pressure method. A dosing port is left on the pipeline before the inlet of the water injection pump. Hydrochloric acid and sodium chlorite, the ratio of the two agents is 1:1 (dosing concentration 140mg/L). Chlorine dioxide is synthesized in the reactor and sterilized by the sewage pipeline to the injection pump.

Negative pressure method. The dosing point is on the pipeline before the inlet of the water injection pump and before the water injection buffer tank. Hydrochloric acid and sodium chlorate, the ratio of the two agents is 3:1 (dosing concentration is 120mg/l), and the chlorine dioxide is reacted in the reaction kettle to be sterilized by the ejector into the sewage pipeline and injected into the injection pump. After the excess gas is recovered, it is injected into the pump through the water injection buffer tank. The experimental results are shown in Table 2.

Table 2. Germicidal efficacy of chlorine dioxide

Sampling point	SRB(mg/l)		TGB(mg/l)		IB(mg/l)	
	Positive pressure method	Negative	Positive pressure method	Negative	Positive pressure method	Negative
Sewage tank outlet	1.3×10^3	9.5×10^3	1.3×10^2	2.5×10^2	1.1×10^4	4.5×10^3
Water injection	0	0	0	0	0	0
A	6.0×10^0	0	6.0×10^1	0	6.0×10^2	0
B	2.5×10^1	0	2.5×10^2	0	1.1×10^4	0
C	6.0×10^0	0	2.5×10^2	0.3×10^0	1.1×10^4	0

During the test, SRB sampling was observed from day 3 to day 9 of three test wells. The data shows that the number of SRBs in the test wells dropped significantly. From Table 2, after 3 days of sterilization by chlorine dioxide, SRB was significantly reduced; the negative pressure method was superior to the positive pressure method, and its (SRB), (TGB) and (IB) killing were close to 100%. And the number of bacteria was not recovered again on the 9th day after the test. Therefore, it is considered that the negative pressure chlorine dioxide sterilization measures are efficient and long-lasting in the sterilization of oil field sewage.

From the two methods of positive pressure method and negative pressure method to produce chlorine dioxide, the negative pressure method has higher conversion rate of chlorine dioxide and better sterilization effect. From Table 3, the negative pressure method has the lowest cost. Therefore, considering the comprehensive consideration, the chlorine dioxide sterilization method of the negative pressure method is better than several other sterilization methods.

Table 3. Effect and cost table of fungicides

Fungicide name	category	Dosing concentration(mg/l)	Dosing method	Tons of water cost (RMB)	Effect (SRB kill rate of water injection wellhead)	Remarks
Ordinary fungicide	-	50	daily	0.36	invalid	
		100	continuous	0.71	limited effect	
High concentration fungicide	-	25	continuous	1.63	Limited effect	
Chlorine dioxide sterilization	Positive pressure method	140	Daily continuous	0.29	Effective	Hydrochloric acid + sodium chlorite 1:1 (450kg: 450kg)
	Negative pressure method	120	Daily continuous	0.21	Effective	Hydrochloric acid + sodium chlorate 3:1 (600kg: 200kg)

3. Chlorine dioxide mixed with polystyrene

3.1. Clear and dirty

Viscosity is a key indicator in the development of polymer flooding, which directly affects the efficiency of polymer flooding after injection into the formation, thus affecting the overall development results of the block. Viscosity is mainly considered from four aspects, namely, in the preparation station, mother liquor pipeline, injection station, single well pipeline viscosity [6-10]. Among them, single well pipeline has the largest proportion of sticking loss. From Table 4, the sticking loss of the single-well pipeline with clear and dirty is obviously higher than that of clearing and thinning. Studies have shown that the viscosity is mainly affected by the reduction of sewage [10-12].

Table 4. Statistical data for viscosity injection of polymer mother liquor

Polymer molecular weight	Mixed mode	In the preparation station(%)	Mother liquor pipeline(%)	Injecting station(%)	Single well pipeline(%)	Full journey(%)
7 million	Clear and thin	2.2	1.7	7.5	10.5	21.9
	Clear and dirty	2.2	1.8	8.2	23.6	35.8
	Difference	0	0.1	0.7	13.1	13.9
25 million	Clear and thin	1.6	1.9	7.3	8.6	19.4
	Clear and dirty	1.9	1.9	8.7	20.1	32.6
	Difference	0.3	0	1.4	11.5	13.2

As mentioned in the previous chapter, chlorine dioxide acts as a strong oxidant and is compatible with water-flooding wastewater. After blending (SRB), (TGB) and (IB) killing is close to 100%. Consider using chlorine dioxide to treat the polymer flooding wastewater, and then use the sewage to dilute the polymer to examine the viscosity change.

The content of SRB and IB of the polymer flooding wastewater treated with chlorine dioxide in the A joint station is shown in Table 5.

Table 5. Properties of test water

Sampling point	SRB	IB
A Union Station before sewage sterilization	6.0×10^3	6.0×10^3
A Union Station after sewage sterilization	0.6	0

Diluted polymer from sterilized sewage, from Daqing Refining & Chemical Co., Ltd. (25 million molecular weight), content 1500mg / L. As shown in Fig. 7, from the viscosity point of view, the chlorine dioxide sterilizing water dilution solution is higher than the non-sterilized water, and its value is equivalent to the dilution of the water. The 20d viscosity retention rates of diluted water, chlorine dioxide sterilizing water and non-sterilized sewage diluted polymer were 82.4%, 83.3% and 72.5%, respectively.

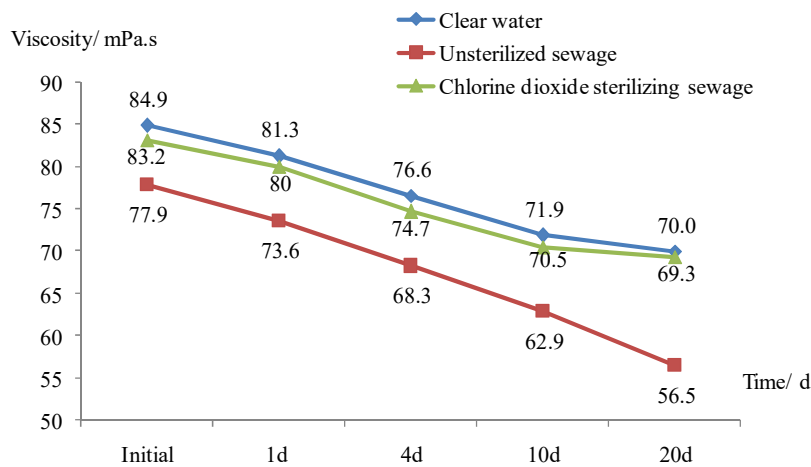


Fig 4. Viscosity variation map of 25 million polymer in clean water - sewage dilution and refining

The use of chlorine dioxide sterilizing sewage to dilute the polymer solution can obtain a higher initial viscosity, which has a small stick loss and a high retention rate.

3.2. Pollution and dilution

Studying the fouling of the solution achieves a good polymer blending effect. In 2018, at the 1#~5# injection station, the experiment of using chlorine dioxide to sterilize the contaminated polymer containing polystyrene was carried out.

The test samples were from refining and chemical conversion of 7 million and 25 million polymers. In the implementation, the comparison of clearing and thinning and fouling is shown in Fig. 8 and Fig. 9.

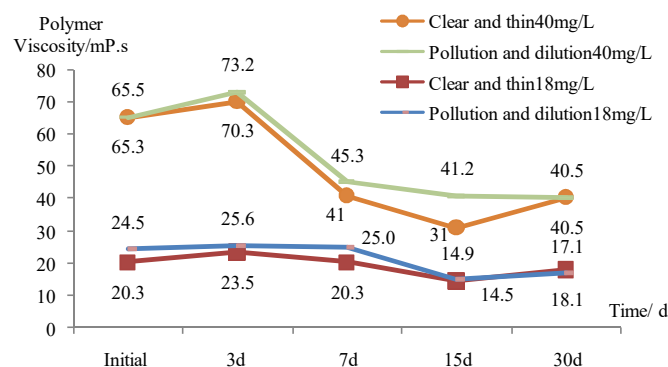


Fig 5. 7 million polymer map for cleaning and thinning and pollution distribution

4. Conclusion

Commonly used ultraviolet, conventional or high-concentration fungicides have certain bactericidal effects in a short period of time, but their effects are not long-lasting, and the amount of test bacteria at the wellhead is restored.

After the chlorine dioxide sterilization, the SRB, TGB and IB in the sewage were significantly reduced. The 9d wellhead sampling showed no recovery of the bacterial amount, and its durability was good. The negative pressure chlorine dioxide sterilization technology was better than the positive pressure method (SRB). , (TGB) and (IB) kill nearly 100%, the lowest cost.

The use of chlorine dioxide sterilization and flooding sewage to clean the contaminated or contaminated polymer, the initial viscosity of the solution is higher, the viscosity is small, the viscosity retention rate is high, and the gap is not much difference.

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