

Research on Environmental Friendly Low Phosphorus Circulating Water Treatment Technology and Its Application

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Abstract:

The paper is based on in-depth study, analysis of new water and return water quality, at the same time to optimize the actual situation of refinery of circulating water system, relevant personnel developed the environmental protection low phosphorus circulating water treatment technology, and used in the reality of refinery circulating water system work. The final research proved that this technology can significantly reduce the low steel test average adhesion rate and average corrosion rate, prove that environmental protection low phosphorus circulating water treatment technology has very high application value, and can make the return water to higher proportion, to a certain extent, reduce the quality of circulating water discharge total phosphorus, making the enterprise to obtain higher comprehensive benefit. In this study, the author will first introduce the main water quality, and then analyze the treatment technology and application of environmentally friendly low phosphorus circulating water.

Keywords:

Low Phosphorus Circulating Water, Low Phosphorus Water Treatment Agent

1. Introduction

At present, most of the chemical fertilizer, chemical industry, ethylene, oil refining enterprises in China's petroleum and petrochemical industry use phosphorus formula as the water treatment agent used in the circulating cooling water system, and even some enterprises use high formula phosphorus content. Although phosphorus is not toxic, it has rich internal effects. After contact with it, the water body is very likely to produce eutrophication problems, leading to the rapid reproduction of algae or other microorganisms in the water, and eventually leading to adverse environmental problems such as seawater red tide and lake water bloom, resulting in the destruction of ecological balance. To achieve the sustainable development goals, related companies need to transform the original high phosphorus or phosphorus formula into a greener water treatment formula.

An enterprise of Sinopec follows the 2015 edition of the "Pollutant Discharge Standard for Petroleum Refinery Industry" to control the discharge of sewage, which

stipulates that the total phosphorus mass concentration below 1 mg/L should be controlled in the external sewage water. According to the analysis of the source of total phosphorus, it can be seen that the enterprise uses the circulating water system based on the phosphorus water-containing circulating water treatment technology to detect the total phosphorus mass concentration of about 3 mg/L in the sewage water. The reason why the phosphorus content discharged from the sewage treatment plant in the oil refining area is mainly caused by the discharge of circulating water. After calculating the total phosphorus of the sewage treatment plant in the refining area, it is learned that the relevant personnel must start from the source, that is, use phosphorus-free corrosion inhibitor or low-phosphorus corrosion inhibitor in the circulating water system, so as to ensure that the sewage discharged from the refining can quickly meet the prescribed standards and improve the comprehensive benefit of the enterprise.

2. Main Water Quality

The supplementary water of the circulating water system of an enterprise of Sinopec is mainly the effluent from the low concentration sewage treatment system after special treatment. The water quality indexes of the new water and reclaimed water are shown in Table 1.

Table 1. Water quality indexes of new water and reclaimed water use.

Item	Reuse water	New water
Scaling factor	0.53	0.06
index of stability	7.81	10.02
index of stability	8.76	1041.26
Total dissolved solid (mg·L ⁻¹)	728.65	76.74
ammonia nitrogen (mg·L ⁻¹)	0.26	-
Positive phosphorus (mg·L ⁻¹)	0.30	0.18
CODCr (mg·L ⁻¹)	44.21	-
total phosphorus (mg·L ⁻¹)	0.50	0.24
Zn ²⁺ (mg·L ⁻¹)	0.67	-
SO ₄ ²⁻ (mg·L ⁻¹)	118.03	8.34
total iron (mg·L ⁻¹)	0.17	0.06
Cl ⁻ (mg·L ⁻¹)	107.86	6.65
total iron (mg·L ⁻¹)	141.46	26.81
Conductivity (Spt·cm ⁻¹)	1056.01	111.21
calcium hardness (mg·L ⁻¹)	104.01	33.86
pH	7.40	7.31

According to the above table, return water has 0.50 mg/L total phosphorus mass concentration, 44.21mg/L CODCr and 0.26 mg/L ammonia nitrogen than new water, which provides a favorable environment for microbial reproduction and growth; return water and new water, which is corrosive; new water has corrosion factors higher than return water, it is more corrosive than new water; in terms of scale factor, the new water is lower than return water, proving that return water has stronger scaling [1]. If the mixed return water and new water are used as supplementary water in the circulating water system, attention must be paid to the control of microorganisms and scaling.

3. Environmental Protection Type of low Phosphorus Circulating Water Treatment Technology

3.1. Overall thinking

In practice, relevant personnel need to complete the configuration of mixed water, the ratio of new water and return water mixed water is 3:7, after the mixed water as the test water, only the rotating plate test to determine the use of various doses and types of scale inhibitor, corrosion inhibitor under the actual effect of various combinations, to determine the best scale corrosion inhibitor.

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3.2. Instruments and reagents for the test

This test will mainly use dynamic simulation experimental device, constant temperature water bath, rotating hanging sheet corrosion instrument, electric mixer and beaker and other instruments.

In terms of test reagents, relevant personnel prepared polyacrylic acid scale inhibitor, diethyl phosphate, acetaldehyde, sodium oxide solution, phosphoric acid, polyaspartic acid, etc.

3.3. Make the polyaspartic acid

In practice, relevant personnel mainly use the following four steps to make polyaspartic acid: first, Prior procurement of aspartate in line with industrial standards, 15g of aspartate was taken during the preparation work, and is placed in a beaker. Then, 5 mL of 88% concentration of phosphoric acid was added to it; next, a beaker in an environment of around 240°C, ensure that the substance in the beaker appears under the action of high temperature; once more, when the formed material is put into the aqueous solution of sodium hydroxide, about 8% aqueous sodium hydroxide, implement the hydrolysis treatment. During hydrolysis, substances should have pH in the range of 9-10; last, remove the hydrolyzed liquid material, to eventually get a red and brown liquid, that is, the winter safety solution [3].

3.4. Make phosphonate-hydroxyacetic acid

There are also four steps for obtaining the product of phosphonyl acetic acid: First, 110g diethyl phosphate, and placed in an acetaldehyde solution at a 45% -55% concentration. The content mass of the acetic acid solution should be 220g, in this case, acetaldehyde solution and diethyl phosphate can react more fully. Then the work is to control the temperature reasonably; next, relevant personnel need to adjust the test temperature in the range of 25-45°C, and the fusion of the two for 2h; once more, relevant personnel should gradually increase the test temperature, the optimal temperature range is 90-110°C. At the same time, continue to stand in this temperature for 4-5h; last, to remove the final reaction product, Brown sticky liquid, that is, phosphine hydroxyacetic acid.

3.5. Make low phosphorus environmental protection water treatment agent

Combined with the investigation results, if the relevant personnel is used alone or phosphine hydroxyacetic acid polyaspartate is difficult to achieve the ideal sewage treatment effect, the economic benefits of related treatment technology is at a low level, in order to help enterprises to obtain higher economic benefits, relevant personnel decided according to the appropriate proportion of mixed polyacrylic acid scale dispersant, polyaspartate and acetic acid, in order to make the water treatment agent scale corrosion suppression effect [4]. Through experimental study, when the ratio of 1:3:1, polyacrylic acid is configured, low-phosphorus environmental protection water treatment agent, that is, RP-18 scale resistance and corrosion inhibitor.

4. Analysis of the Test Results

4.1. Analysis of corrosion suppression effect

Table 2 shows the actual corrosion inhibition effect of RP-18 at various concentrations. Combined with this table, it can be seen that when the relevant personnel use RP-18 with a mass concentration above 70 mg/L, the corrosion rate below 0.015mm / a can be controlled, which proves that the corrosion inhibition effect of the treatment agent is more prominent.

Table 2. Actual corrosion inhibition effects of RP-18 at various concentrations.

Pharmacy quality concentration (mg·L ⁻¹)	Rate of corrosion (mm·a ⁻¹)
120	0.005
110	0.007
100	0.008
90	0.009
80	0.010
70	0.015

4.2. Analysis of scale resistance effect

The effects of RP-18 in stabilizing zinc, calcium carbonate scale, and stabilizing phosphorus are shown in Table 3. According to this table, when the RP-18 of 80-120 mg/L mass concentration is used, the control test water is 418 mg/L calcium hardness and 548 mg/L total supervision, and the probability of stabilizing zinc, calcium carbonate scale and stable phosphorus are 62.52%, 98.34% and 78.76% respectively, which plays a relatively ideal scale resistance effect.

Table 3. RP-18 in stabilizing zinc, calcium carbonate scale and stabilizing phosphorus.

Pharmacy quality concentration (mg·L ⁻¹)	Zinc steady rate (%)	Blocking calcium carbonate scale rate of (%)	The phosphorylation rate was (%)
120	75.31	100.00	90.04
110	72.58	99.03	85.12
100	70.04	98.01	82.03
90	65.14	98.71	19.01
90	62.52	98.34	78.76

4.3. Analysis of the dynamic simulation results

The ratio of 3:7 to mix new water and return water as the supplementary water used in the dynamic simulation test, without seeing the prefilm treatment of the test tube,

the outlet temperature of 40-42°C, the flow rate of 0.8-1.0m/s, 32 °C inlet temperature, 4.8-5.2 concentration multiple, and organophosphorus [6] brought by 1.08-1.32mg/L agent. When the test conditions were used for 15d, the circulating water quality data shown in Table 4, such as carbon steel tube adhesion and corrosion condition [5] shown in Table 5. The final result proves that the system can operate smoothly under such test conditions, and the adhesion rate and corrosion rate of carbon steel test pipe are at low levels.

Table 4. Recycling water quality data.

Project	Crest value	Minimum value	Average value
cycles of concentration	5.33	4.88	5.04
Positive phosphorus (mg·L-1)	2.98	2.25	2.48
total phosphorus (mg·L-1)	4.43	3.84	4.15
Organophosphonates brought by the agent (mg·L-1)	1.35	1.01	1.22
SO ₄ ²⁻ (mg·L-1)	313.19	253.99	180.67
total iron (mg·L-1)	0.40	0.29	0.34
Cl ⁻ (mg·L-1)	493.39	416.69	451.24
total alkali (mg·L-1)	348.49	311.59	329.19
Conductivity (Spt·cm-1)	2999	2809	2881
calcium hardness (mg·L-1)	229.00	209.00	216.40
pH	9.89	8.65	8.78

Table 5. Results of the dynamic simulation tests.

Project	Parameter
The adhesion rate of the test tube (mg·cm-1·m-1)	1.1299
110 (mm·a-1)	0.0089

4.4. Wordness test

The scale resistance and corrosion inhibition effects of RP-18 when using trichloroisocyanuric acid, isothiazolinone, and 1227 are shown in Table 6. According to the table, it can be seen that the fungicide will not affect the corrosion inhibition effect of RP-18, but it will weaken its scale resistance effect, mainly because of the oxidation characteristics of the fungicide, which can improve the decomposition speed of organic phosphonate, thus leading to more orthophosphorus in the solution. Because the phosphorus content of RP-18 agent is low, the adverse effects of fungicide are largely avoided.

Table 6. Effect of RP-18 in fungicides.

Medicamentt	Stable phosphorus rate (%)	Calcium carbonate scaling rate (%)	Zinc steady rate (%)	Corrosion rate (mm·a-1)
RP-18	82.01	99.01	90.08	0.010
symclosene +RP-18	79.31	97.63	67.21	0.011
isothiazolinone+RP-18	82.01	97.73	68.32	0.010
1227+RP-18	79.31	97.63	67.21	0.011

At the same time, relevant personnel also analyzed the influence of RP-18 on fungicides. The details are shown in Table 7, which proved that RP-18 has good compatibility with various fungicides and can play an important role in controlling the reproduction, corrosion and scaling of circulating water microorganisms [7].

Table 7. Results of the sterilization test.

Antiseptic	Bactericidal rate when used alone (%)	The ization rate when coordination with RP-18 (%)
Symclosene	99.99	99.99
Isothiazolinone	82.41	82.41
1227	93.21	91.41

5. Practical Application Effect

During the three-month RP-18 industrial experiment, significant water-saving effect was achieved, and the proportion of recycled water consumption increased to an astonishing 77.23%, which was equivalent to increasing the recycled water consumption by 165432m³, saving the same amount of fresh water and sewage, that is, 165432m³, thus saving the cost of new water and sewage, saving a total of 183,600 YUAN. At the same time, by optimizing the sewage treatment process, the input of polyaluminum chloride phosphorus removal agent is reduced, which directly saved the drug cost of 43,400 yuan.

In terms of energy saving, the operating cost of sewage treatment equipment has been successfully reduced, and by reducing the operation of a water pump, an amazing 51,100 yuan of power expenditure every year. The sum of these direct economic benefits reached 2,78,100 yuan.

More importantly, the total phosphorus mass concentration of circulating water discharge decreased from 10 mg/L to only 3 mg/L, with a decrease of up to 70%. With an external displacement of 25 cubic meters per hour, the total phosphorus discharge of the entire circulating water system was reduced by 42.84 tons. Such environmental protection achievements have brought significant social benefits and are highly in line with the sustainable development goals of enterprises.

6. Conclusions

To sum up, the application effect of this environmental protection low phosphorus circulating water treatment technology is significant, which not only realizes high efficiency scale resistance and corrosion inhibition, but also optimizes the compatibility of fungicides, so as to improve the stability and reliability of the circulating water system. Through practical application cases, we find that this technology can significantly improve the utilization rate of reuse water, reduce the consumption of new water and sewage volume, and save a lot of costs for enterprises. At the same time, the technology also effectively reduces the total phosphorus content, and plays a positive role in environmental protection.

Conflicts of Interest

The author declare that there is no conflict of interest regarding the publication of this article.

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