Study on the Effect Of SO_4^{2-} Ion on the Scale Inhibition Performance of Water Stable Medicament

Jinying Wu [1, a], Min Zhang [2, b] , Changshan Huang [3, c],
Caixia Sun[4, d] and Min Chen[5, d]

[1,2,3,4,5]Institute of Energy Research, Henan Academy of Science, No.29 Garden Road, Zhengzhou R.P.China, 450008

[a]251093375@qq.com , [b]515725785@qq.com, [c]13937140170@163.com

[d]caixiasun@alum.imr.ac.cn , [e]279545960@qq.com

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Abstract: This article by joining the 20ppm water stable medicament in the standard water sample and the different dosage the SO_4^{2-} ion , carry on the scale inhibition performance and the electronic scanning test, and concluded that inhibiting performance plummets with the increase of the amount of SO_4^{2-} ion, and explains SO_4^{2-} ion has an effect on inhibition of water stabilizer.

Introduction

In industrial cooling water systems, due to cooling water evaporates constantly, need to continue to add water, thus making the salts in the water are concentrated**,** and its hardness, alkalinity, calcium and chloride ion concentration increase, leading to circulating cooling equipment scaling , corrosion and the low efficiency of heat exchange, not operate normally, in order to solve this problem, we need to process the water quality. The most commonly used method is added to the the water quality stabilizer which has the scale, corrosion inhibition and biocide to prevent its scaling, corrosion and bacteria and algae growth. While the supplemental water is tap water, which mainly contains Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^-, Cl^- and a small amount of SO_4^{2-}. In water treatment former research, we explore the factors influencing the scale inhibition performance of water quality stabilizer, often considered Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^- ; discusses the factors which influence the performance of corrosion, thinks of Cl^- and SO_4^{2-}, and the SO_4^{2-} ion on the properties of water quality stabilizer anti-scaling effect research is very few, so in some factories and power plants, because of the limitation of drainage, the cooling circulating water are often used in high concentration ratio, high alkalinity and high Ph, not normal play to scale inhibition effect of water quality stabilizer.In order to increase the solubility of calcium carbonate and prevent scale formation [1, 2], we often adjust them with sulfuric acid. Although the corrosion inhibition performance of water stabilizer itself can reduce corrosion of sulfate ion to metal, but it does affect the scale inhibition performance of water quality stabilizer.

The Experimental Part

Testing instrument. KZC-1 type fast scaling inhibition instrument, Manufacturing China Qinyou Instrument Factory; Jsm-6510 scanning electron microscope, the Japanese Electronics Co. production.

Experimental reagents. anhydrous calcium chloride solution (0.1359mol/L $CaCl_2$), sodium bicarbonate solution (0.2812mol/L $NaHCO_3$), EDTAsolution (0.0107 mol/L), potassium sulfate solution(30mg/ml). the water quality stabilizer is composed of hydroxy ethylidene diphosphonic acid (HEDP), polymaleic anhydride (HPMA), polyacrylic acid (PAA) and Benzotriazole (BTA) compounded, dosage is 20mg/L .

The test of water. Test water used for simulation of standard water solution, calcium ion concentration is 80 mg/L, Ph is 6.5 (test paper measurement).

Testing method.

Inhibitors preparation testing.HG/T 2024—1991 determination of scale inhibition performance of water treatment agents----- bubble method [3]: The 20ppm water stabilizer were added in the standard water solution, then added to 300ppm, 600ppm, 900ppm, 1200ppm, 1500ppm SO_4^{2-} ion solution in it respectively, in the bubbling gas flow rate of 80 L/h, 60°Cwater bath conditions, constant temperature of 6h,and the blank test at the same time , finally shut off the power supply, the test solution was cooled to room temperature, determination of the stability of calcium ion concentration in water samples, the analysis methods are as follows.

With the pipette aspiration of a certain volume of water sample after experiment in conical flask, adding 20% potassium hydroxide and calcein-phenolphthalein mixed indicator, on a black background with EDTA standard solution titration. calculation formula is as follows

$$X = \frac{M\times(V_1-V_0)\times 40.08}{V}\times 1000 \qquad (1)$$

X------- the concentration of calcium ion stability , mg/L
M ------- the molar concentration of EDTA standard solution, mol/L
V_1 ------ consumption volume of EDTA standard solution . mL
V_0 ------ titration blank solution, the consumption of EDTA standard solution volume, mL;
V --------- water volume, mL;
40.08 ----- the atomic mass of calcium

Expressed as a percentage of the water treatment agent inhibition rate (&), calculation formula is as follows

$$\&=\frac{X_2-X1}{80-X_1} \qquad (2)$$

X_1--------- The stability concentration of calcium ion of blank sample
X_2------- The stability concentration of calcium ion of test sample, mg/l
80------- concentration of the calcium ion in water standard, mg/l

Scanning electron microscope test of the experimental production . Put the scale inhibition test sample solution into the constant temperature water bath, evaporation temperature is 85°C, and then spray gold on the solids, were tested by scanning electron microscope.

Results and Discussion

SO_4^{2-} ion in different adding amount of scale inhibition rate of experiment. According to the industrial circulating cooling water treatment design code GB50050 - 2007[4], rules on indirect open system of circulating cooling water quality indexes of SO_4^{2-}+Cl^- is less than or equal to 2500 mg/l, at the same time, according to Cl^- ion content of the tap water in the local water supply in general 70-90 mg/l, has made the SO_4^{2-} 300ppm, 600ppm, 900ppm, 1200ppm, 1500ppm adding amount of the experiment. the experimental results are as follows.

Table 1 the experimental results of scale inhibition rate

Adding amount of SO_4^{2-} ion (ppm)	0	300	600	900	1200	1500
Inhibition rate of Ca^{2+} (%)	88.14%	80.69%	78.83 %	78.03 %	77.09 %	76.42 %
Remarks	Water quality stabilizer addition is 20ppm, the content of calcium ion in water standard is 80mg/l, the Ph value is 6.5					

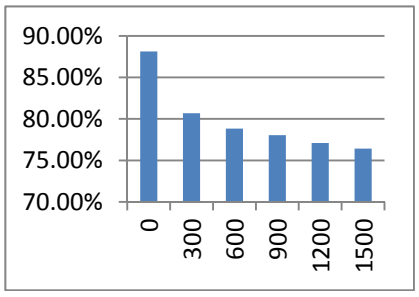

Fig.1 Inhibition rate of different SO42- ion amount

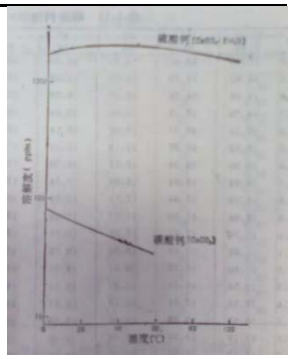

Fig. 2 solubility of calcium sulfate and calcium carbonate of comparison

From Table 1 and Figure 1, we can see that, after the addition of 20ppm water stabilizer in standard aqueous solution, then were added to 300ppm, 600ppm, 900ppm, 1200ppm, 1500ppm SO42- ion solution espectively. The scale inhibition rate compared with the solution without SO42– ion, the downward trend is linear, its scale inhibition rate fell from 88.14% to 76.42%, Thus SO42- ion have influence on the scale inhibition performance of water quality stabilizer.

Electronic scanning result.

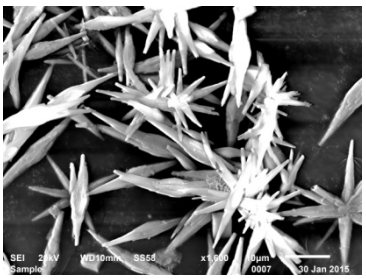

Fig. 3 Blank test product

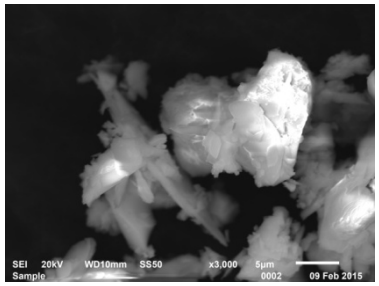

Fig. 4 Containing water stabilizer product

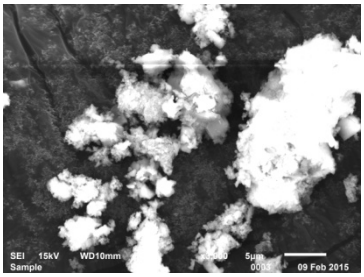

Fig. 5 water stabilizer + 1500mg /l SO_4^{2-} product

Figure 3 is a scanning electron figure without adding water treatment agent and SO_4^{2-} blank scale performance testing product, it can be seen from the figure, the product of calcium carbonate showed a uniform distribution of the leaf shape; Figure 4 is a diagram of the electronic scanning plus water treatment agent without adding SO_4^{2-} scale performance testing of the product, it can be seen from the figure, the shape of calcium carbonate has changed, due to the role of inhibitor**,** the majority of form mushroom product**,** small part because of the role of scale inhibitor, but also to maintain the original shape of calcium carbonate ; Figure 5 is a diagram of a scanning electron plus water treatment agent and SO_4^{2-} scale performance testing of the product, it can be seen from the figure**,** due to scale effects**,** most of product form a smaller mushroom shape.

The reason and analysis. From the solubility point of view, we know that the solubility of calcium carbonate is less than calcium sulfate (see Fig. 2). Calcium sulphate in water mainly exist in ion state , scaling tendency is smaller than calcium carbonate. Calcium concentration and sulfate ion concentration (mg / l) of the product is usually not more than 500,000 (i.e. $[Ca^{2+}] \times [SO_4^{2-}] < 5\times10^7$) **,** opportunities for the formation of calcium sulfate is very small [5]. In this experiment, the

maximum value of $[Ca^{2+}] \times [SO_4^{2-}]$ is 80 × 1500 = 90000 (mg / l), therefore, calcium sulfate is not caused the decrease of scale inhibition performance of water stabilizer.

From the scale and dispersion stabilizer mechanism, organic phosphonic acid and poly-carboxylic acid has compatibilization and lattice distortion. Compatibilization performance can be ionized H^+ and negatively charged ions in the water, the difference is that organic phosphonic acid molecular weight is small, ionized ions and Ca^{2+}, Mg^{2+} and other metal ions form stable complexes, improved the calcium carbonate crystal grain saturation, increase the solubility of calcium carbonate, reduce scale formation, making it has good scale inhibition ; poly-carboxylic acid because of large molecular weight, the molecular chain of the anion of ionization and strong adsorption, their adsorption on some impurity ions, making it has the very good dispersion [6]. The function of the lattice distortion is that organic phosphonic acid molecules are adsorbed on the active growth of calcium carbonate crystals and Ca^{2+} chelation, inhibiting the growth of the movement direction of the lattice, make the lattice deformate, played the role of scale inhibition; poly-carboxylic acid is a linear polymer, which is adsorbed on the calcium carbonate crystals at one end, the rest of the surrounding around the crystal, make it not grow, play a role in the dispersion scale. Due to the addition of SO_4^{2-} with two negative charges, does not have the adsorption effect, but it can produce attraction to calcium, reduce the rate of Ca^{2+} and chelating organic phosphinic acid, which reduce the scale inhibition performance of water stabilizer.

Summary

In summary, SO_4^{2-} has an effect on the scale inhibition performance of water quality stabilizer , when the cooling circulating water Ph was adjusted with acid, sulfuric acid should be avoided so as not to affect the performance scale water stabilizer

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