New Estimation of the Dosage of Scale Inhibitor in the Cooling Water System

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Abstract: In the cooling water system, excessive use of organic phosphate scale inhibitors is harmful to environment. Reducing the dosage of the organic phosphate scale inhibitor is important. A self-made jacketed crystallizer was used in this experiment. The critical pH values have been determined in cooling water systems with series of Ca^{2+} concentrations by adding different concentration of the scale inhibitor ATMP (Amino Trimethylene Phosphonic Acid) according to the calcium carbonate Metastable zone theory. A model equation at 45 ^{o}C and pH=9 was proposed to estimate the lowest dose of the scale inhibitor ATMP. The measured pH value was approximate to the expected pH value in two cooling water systems through verification test.

Keywords: Metastable zone, Critical pH, Scale inhibitor dosage

Introduction

Normally, using phosphonates as inhibitors is a effective method of preventing mineral scale and corrosion in cooling water systems[1,2]. Excessive using the scale inhibitor can reduce scale information risk[3]. But this brings environmental problems. A number of non-toxic, low phosphorus and phosphate-free chemicals is developed environment-friendly[4]. However, there still is no phosphate-free scale inhibitor to replace the traditional organic phosphate scale inhibitor[5]. Therefore, how to control strictly the dosage of organic phosphate scale inhibitor is important.

In cooling water system, calcium carbonate is the predominant component of scales deposited in cooling water systems[5-8]. Chemical crystallization is one of the important scale formation causes. Theoretically, nucleation should initiate when solute concentration passes the saturation point and the solution becomes supersaturated. However, this does not occur instantly and solute remains in solution until a sufficiently high level of supersaturation is generated to induce spontaneous nucleation[9]. Wilhelm Ostwald called this unstable state of labile region. Between this region and the solubility curve is known as metastable zone[10,11].

The scale inhibitors can broaden the width of metastable zone[11], increase the induction time, inhibit crystal growth[12] and change the morphology of crystalloids[13,14]. In different cooling waters, adding different concentrations of inhibitors, $CaCO_3$ crystallization metastable zone width will inevitably different. In the actual cooling water system, only when the operating conditions are controlled within the crystallization metastable zone, the scale inhibitors could do work.

Based on the calcium carbonate metastable zone theory, by the critical pH method[15-17], an attempt at the quantitative relation between scale inhibitor ATMP concentration and Ca^{2+} concentration has been made under 45 °C and pH=9 and a model equation was observed. This would avoid deciding the inhibitor dosage only by experience. The calculated dosage by the model could meet the needs of not only inhibiting the scale formation but also limiting the dosage of organic phosphate scale inhibitor.

Experimental

Figure 1 is the design drawing of self-made jacketed crystallizer. The schematic drawing of experimental apparatus for cooling water system is in Figure 2.
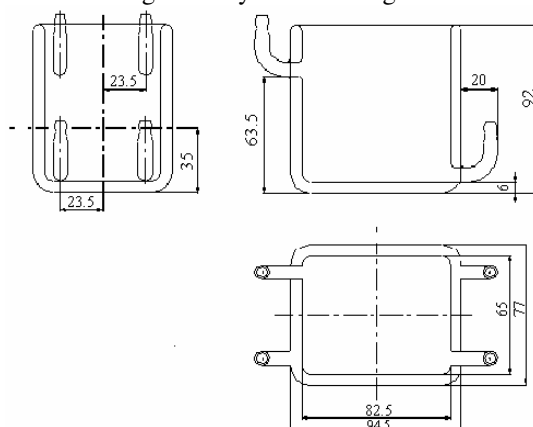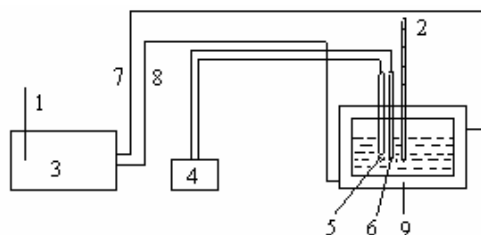

Figure 1. The design drawing of self-made jacketed crystallizer

1, Thermometer; 2, Thermometer; 3, Super constant temperature water-bathing; 4, Acidometer; 5, Glass electrode; 6, Reference electrode; 7, Outlet line of crystallizer; 8, Inlet line of crystallizer; 9, Jacketed crystallizer

Figure 2. The sketch of experimental setup

Series concentrations (Table 1) of $CaCl_2$ and $NaHCO_3$ stock solutions were prepared and used to simulate the cooling water. Equal volume of the both stock solutions were added into a 500 mL jacketed crystallizer with a super constant temperature water-bathing to control temperature accuracy of ±0.5 °C and the solution was mixed by a magnetic stirrer

at a constant speed. A metering pump was used for pumping 0.1 mol- L^{-1} NaOH solution at the speed of 0.05 mL.min^{-1}. A pH sensor was used to show the solution changes during crystallization process.

Table 1. Series concentrations of stock solution

Stock solution	Series 1	Series 2	Series 3	Series 4	Series 5
CaCl$_2$, mmol- L^{-1}	6.000	9.000	12.01	14.01	20.01
NaHCO$_3$, mmol- L^{-1}	13.80	21.15	27.60	32.90	47.78
Ca^{2+} concentration in simulate cooling water, mmol- L^{-1}	3.000	4.500	6.005	7.005	10.01

The sets of experiments consisted of putting 200 mL simulate cooling water and the CaCO$_3$ inhibitor ATMP(Amino Trimethylene Phosphonic Acid) into the thermostated vessel of 500 mL and after the temperature stabilizing at 45±0.5 ^{o}C, titrating the 0.1 mol.L^{-1} NaOH solution at the speed of 0.05 mol. L^{-1}. The solution pH value was read during crystallization processes.

Results and Discussion

Critical pH value measurements

The critical pH value in different simulate cooling water system was affected by concentrations of inhibitor ATMP. The diagram in Figure 3 shows the effect of the inhibitor ATMP concentrations on the Critical pH value in several systems containing different concentrations of Ca^{2+} at 45 ^{o}C.
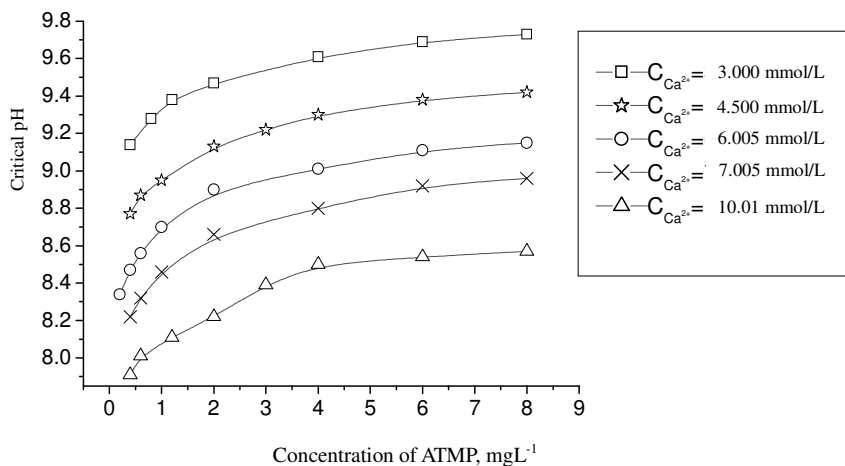

Figure 3. Variation of critical pH with ATMP concentration in several cooling water containing different concentrations of Ca^{2+}

In order to find the quantitative relations of the critical pH values and the concentrations of ATMP (C_{ATMP}), a plotted was drawn (Figure 4) between lnC_{ATMP} and critical pH. In the cooling water system with the same concentration of Ca^{2+}(C_{Ca}^{2+}), the linear relation between the critical pH value and the concentration of ATMP can be obtained from Figure 3. That is the higher concentration of inhibitor ATMP, the higher critical pH value and wider metastable zone in a certain Ca^{2+} concentration cooling water system
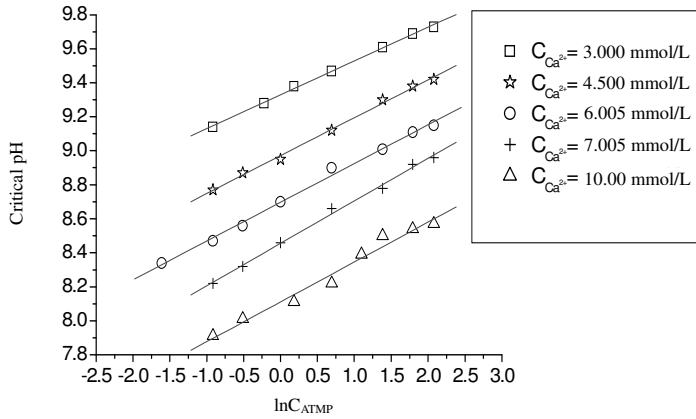
Figure 4. The plot of critical pH against natural logarithms of C_{ATMP} at 45 ^{o}C

Modeling of the estimation for ATMP concentration

The actual plant process systems usually were controlled at a relatively stable pH value, while the concentration of Ca^{2+} was varied with the makeup water. Different system needs different inhibitor concentration. It was even necessary to find the relation between the concentration of Ca^{2+} and that of inhibitor ATMP for estimating the inhibitor dosage.

According to Figure 5, the theoretical relationship between the concentration of ATMP and that of Ca^{2+} could be obtained as the following fitted equation at pH=9.0 and 45 ^{o}C:

$$\ln c = -6.65 + 4.41 \ln c_{Ca}^{2+}.$$

So in a cooling water system with relatively stable Ca^{2+} concentration, the inhibitor ATMP dosage can be estimated quantificationally by the model: $C_{ATMP} = \exp(-6.65 + 4.41 \ln c_{Ca}^{2+})$, which would ensure to avoid estimating inhibition dosage by experience empirically and roughly.
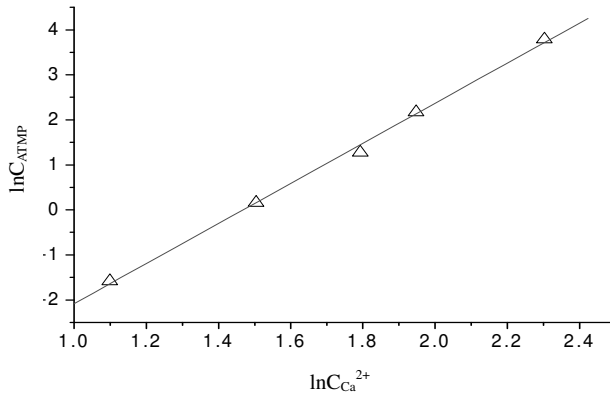

Figure 5. The plot of natural logarithms of C_{ATMP} against natural logarithms of C_{Ca}^{2+} at 45 ^{o}C and pH=9.0

Verification test

The model was applied in two systems with two kinds of Ca^{2+} concentrations. One was 4.000 mmol.L^{-1} and the other was 8.000 mmol.L^{-1}. Assumed that the critical pH value 9.0 was expected, the model calculated dosage ATMP was added into the system. Then the critical pH values were measured. Table 2 shows that the measured critical pH value is very close to the expected.

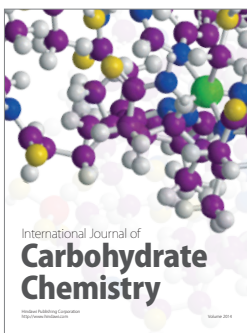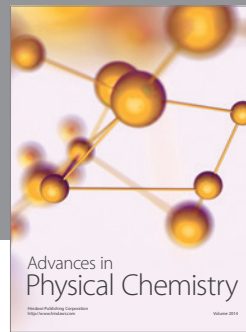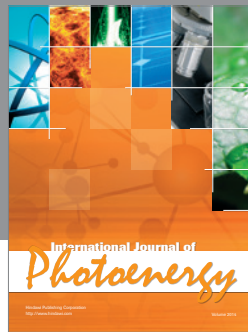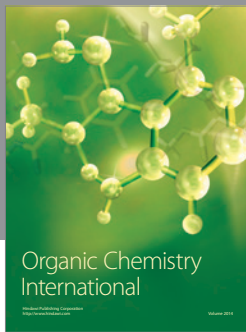**Table 2**. Measured and expected pH value in two systems

Parameters	I	II
Ca^{2+} concentration mmol.L^{-1}	4.000	8.000
Theoretical critical pH value	7.81	7.66
ATMP calculated concentration, mg.L^{-1}	0.58	12.4
Expected critical pH value	9.0	9.0
Measured critical pH value	8.89	8.60
Relative deviation, %	1.22	4.4

Conclusion

The $CaCO_3$ crystal metastable zone has been studied by critical pH method in the self-made jacketed crystallizer. And the theoretical model was derived for the estimation of inhibitor ATMP dosage in cooling-water system by considering the Ca^{2+} concentrations, temperature, pH value. Verification test results showed that the relative deviation between the measured and expected critical pH value was 1.22% and 4.4% after adding the model calculated ATMP concentration into the cooling system. It should be possible to apply the model-building method in order to estimate the other kind of inhibitor dosage to cooling-water system, which not only could save the running cost but also decrease the releasing of phosphoric contaminants.

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