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Comprehensive utilization of phosphate in a highly concentrated recirculating cooling water system using secondary-treated municipal wastewater as make-up

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ABSTRACT

A comprehensive utilization process using phosphate was developed for the reuse of high hardness secondary-treated municipal wastewater to a highly concentrated recirculating cooling water system (RCWS). It showed that the soluble phosphate in the wastewater could be directly reused as a corrosion inhibitor to prevent the RCWS from severe corrosion caused by the contaminants in the wastewater. Based on the synergetic corrosion inhibition of PO_4^{3-} and Zn^{2+}, a chemical program was achieved for recirculating cooling water treatment. It contains 1-hydroxyethylidene-1,1-diphosphonic acid, polyepoxysuccinic acid, zinc sulfate heptahydrate, and a copolymer dispersant of LN-104B. In addition, LN-104B was verified to have excellent inhibition capability to calcium phosphate scale and zinc salts scale in the bench experiments. The pilot-scale experimental results showed that the simulated RCWS operated very well under the condition of high Ca^{2+} concentration (1,500 mg/L as $CaCO_3$) using the chemical program and automatic pH-controlled technique. The corrosion rate and the adhesion rate of the test tubes are only 0.023 mm/a and 2.32 mcm, respectively, which perfectly meet the requirements of the international standard of ISO 16784-2006. Not only can the process cut down the operating cost of RCWS, but also can reduce the environmental risk caused by excessive emission of phosphate. Moreover, large amounts of fresh water and phosphorus resources are expected to be conserved.

Keywords: Phosphate; Secondary-treated municipal wastewater; Comprehensive utilization; Corrosion; Recirculating cooling water system (RCWS); Make-up

1. Introduction

With economic development and rapid urbanization, water resource demand in China is increasing constantly. Water shortages have become a main restriction for China's sustainable development [1]. In recent years, many wastewater reuse projects were established in China [2,3], and reclaimed water, including reliable secondary-treated wastewater and tertiary-treated wastewater, have been reused in many

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aspects, such as landscaping, toilet flushing, and firefighting. Since industries, especially refineries, petrochemical plants, electrical power plants, and steelworks, consume a huge quantity of fresh water in China, to use reclaimed water as an alternative to fresh water in these industries can be expected to save a lot of fresh water resources for other uses.

As we know, on average about 60% of industrial fresh water goes into recirculating cooling water systems (RCWSs), and this percentage rises to 80% for petrochemical plants. Generally, RCWSs are the best users for reclaimed water in industries [4,5]. However, there are many barriers using reclaimed water as make-up water in industrial RCWSs [6–10], and it will be more difficult to achieve reclaimed water reuse in highly concentrated RCWSs.

The characteristics of reclaimed water are quite different from that of fresh water. There are many contaminants in reclaimed water, even if their concentrations are very low, which will pose a strong tendency to form biofilm in RCWSs [11]. The biofilm is widely acknowledged to lead to severe metal corrosion and scale formation [12,13]. Particularly, the phosphate that is commonly found in reclaimed water not only provides an important nutrient to the biofilm, but also tends to form calcium phosphate scale directly. From this perspective, phosphate is a negative factor in recirculating cooling water treatment. However, phosphate also has positive effect on recirculating cooling water treatment, and it had been used as an efficient inhibitor for preventing RCWS from corrosion half a century before. Additionally, phosphate is very precious as a fertilizer in modern agriculture, and the phosphate rock using to manufacture phosphorus fertilizer is a non-renewable resource, whose current global reserves may be depleted in 50–100 years [14]. Thus, to effectively utilize the phosphate in reclaimed water not only will the cost for corrosion inhibitors and the phosphate emission to the environment decrease significantly, but also will the rare phosphorus resources be saved.

In recent years, in order to save more water resources in Chinese industries, the RCWSs have to be operated quite efficiently to concentrate the recirculating cooling water as highly as possible [15–19]. Actually, that is very challenging for the RCWSs in northern China where the calcium hardness of the water is high. Taking the water in Beijing, for example, normally its Ca^{2+} concentration is up to 150 mg/L (as $CaCO_3$). In some areas of the city, it even reaches 300 mg/L. The calcium carbonate scale, therefore, forms frequently when the water is concentrated in the RCWSs, and the calcium phosphate scales out even more easily than calcium carbonate in these systems due to its much lower solubility. For comprehensively utilizing the soluble phosphate as a corrosion inhibitor in the reuse of reclaimed water to RCWS, the phosphate precipitation should be avoided as much as possible.

In the past few years, a novel recirculating cooling water treatment process—pH-controlled process (or acid-dosed process) had been applied in some Chinese industrial RCWSs [17–19]. It successfully increased the cycle of concentration of the RCWSs by decreasing the bicarbonate alkalinity in the water. So far, some systems in Chinese petrochemical plants have been able to operate under the condition of the Ca^{2+} concentration of 1,500 mg/L [18] and still meet the corrosion inhibition requirement (the corrosion rate need to be below 0.075 mm/a) [20], though the RCWSs exhibit less resistant to the corrosion than before when the natural pH process [16,21] was widely used. It was a significant improvement for the recirculating cooling water treatment. But there is still a long way to go to use reclaimed water as make-up in these highly concentrated systems for the reasons we stated above.

The aim of present research is to develop a package of processes for reusing reliable secondary-treated municipal wastewater to the highly concentrated RCWS in a petrochemical plant, and especially for the phosphate in the wastewater to be utilized comprehensively. The eutrophication caused by excessive phosphate emission has been widely viewed as a concern for a long time by many environmental researchers, and various methods for phosphate removal, reclamation and reuse, including absorption [22], ion exchange [23], membrane [24], precipitation [25], and biological treatment [26], have been investigated and proposed. But until now, there has been no report on phosphate reuse from reclaimed water directly.

2. Materials and methods

2.1. Secondary-treated municipal wastewater

A secondary-treated municipal wastewater effluent (i.e. Orbal oxidation ditch followed by secondary clarification) was collected at Fangshan Chengguan Wastewater Treatment Plant located in Beijing from March to October in 2013, and its characteristics in the experimental period were determined using the appropriate standard test procedures [27] listed in Table 1. The characteristics of fresh water which were used as the make-up in an actual RCWS of SINOPEC Beijng Yanshan Company were also provided as a comparison.

As shown in Table 1, the Ca^{2+} concentration of the secondary-treated municipal wastewater is close to

Table 1
The characteristics comparison of secondary-treated municipal wastewater and fresh water

Water characteristics	Secondary-treated municipal wastewater			Fresh water
	Maximum	Minimum	Average	
Ca^{2+} ($mgCaCO_3/L$)	287.5	181.4	248.8	158.7
Total hardness ($mgCaCO_3/L$)	447.0	258.3	367.9	198.3
Total alkalinity ($mgCaCO_3/L$)	340.0	125.8	225.0	145.8
Cl^- (mg/L)	193.0	67.0	118.8	32.3
SO_4^{2-} (mg/L)	295.9	47.2	146.8	45.5
Total iron (mg/L)	1.07	0.02	0.19	0.03
Total phosphorus ($mgPO_4/L$)	4.27	0.23	2.09	ND
Orthophosphate ($mgPO_4/L$)	3.84	0.12	1.80	ND
Conductance (μS/cm)	1,439	782	1,053	627
pH	7.90	7.18	7.55	7.65
Turbidity (NTU)	22.0	3.2	6.1	ND
COD_{Cr} (mg/L)	88.5	5.8	32.3	ND

300 mg/L. Based on the efficiency of the pH-controlled process, the cycle of concentration of the RCWS can only reach 5.0 (the Ca^{2+} concentration of the system is about 1,500 mg/L) when the wastewater is used as make-up. The Cl^- and SO_4^{2-} concentration and the conductivity of the secondary-treated municipal wastewater are all higher than that of fresh water, which indicates that the wastewater is more corrosive than fresh water. Above all, the average phosphate content of the secondary-treated municipal wastewater is up to 1.8 mg/L, and it will be close to 9 mg/L if the wastewater is concentrated five times in the RCWS. Such a high content of phosphate will easily induce calcium phosphate scaling.

2.2. Cooling water treatment chemicals

In the experiments, a 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) was used as an organic corrosion inhibitor, and polyepoxysuccinic acid (PESA) was used as a scale inhibitor. These two inhibitors were both produced by Changzhou Jingke Xiafeng Fine Chemical Co. Ltd. (Jiangsu, China), and their active matter content was more than 50% (wt.). Zinc sulfate heptahydrate was used as a synergistic corrosion inhibitor, and it was an analytical grade reagent made by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Sodium dihydrogen phosphate, also an analytical grade reagent made by Sinopharm Chemical Reagent Co. Ltd., was used to prepare the experimental solutions of different phosphate contents. Four dispersants used in the experiments are all water-soluble acrylic acid/2-acrylamide-2-methylpropanesulfonic acid (AA/AMPS) copolymers with a solid matter content of more than 30% (wt.). Their trademarks and manufacturers were as follows: (1) LH-304, Langfang Aotai Chemicals Co. Ltd. (Hebei, China); (2) ZF322(A)MS, Luoyang Qianglong Industry Co. Ltd. (Henan, China); (3) JC-3211, Changzhou Jingke Xiafeng Fine Chemical Co. Ltd. (Jiangsu, China); and (4) LN-104B, Changzhou Global Chemicals Co. Ltd. (Jiangsu, China). Additionally, sodium dichloroisocyanurate (SDIC) was used as the biocide in the pilot-scale experiment which was produced by Shandong Taihe Water Treatment Co. Ltd. (Shandong, China).

2.3. Bench experiments

2.3.1. Calcium phosphate scale inhibition

The calcium phosphate scale inhibition performances of the dispersants were tested by two methods at different Ca^{2+} concentrations. For the first method [28], the initial Ca^{2+} concentration of the experimental solution was 250 mg/L. The solution was prepared with anhydrous calcium chloride, dihydrogen phosphate, and deionized water at an initial PO_4^{3-} concentration of 5 mg/L, which was buffered by sodium borate to a pH range of 9.1 ± 0.1 for preliminarily evaluating the calcium phosphate scale inhibition performance under a simulative condition of natural pH. A dispersant was added into the solution which was metered in a volumetric flask of 500 mL. The flask then was put into a ZK-1 constant temperature water bath (Jiangsu Gaoyou Instrument Factory, China) at a constant temperature of 80°C for 10 h. After the flask was cooled to room temperature, the residual PO_4^{3-}

concentration of the supernatant was analyzed by spectrophotometry [27]. A 7230 spectrophotometer (Shanghai Analytical Instrument Factory, China) was used to measure the absorbance at the wavelength of 710 nm. The calcium phosphate scale inhibition efficiency was calculated from the following equation:

$$\text{Inhibition } (\%) = \frac{[\mathrm{PO_4^{3-}}]_r - [\mathrm{PO_4^{3-}}]_0}{[\mathrm{PO_4^{3-}}]_i - [\mathrm{PO_4^{3-}}]_0} \times 100\% \tag{1}$$

where $[\mathrm{PO_4^{3-}}]_r$ is the residual $\mathrm{PO_4^{3-}}$ concentration in the supernatant in the presence of the inhibitor, $[\mathrm{PO_4^{3-}}]_0$ is the residual $\mathrm{PO_4^{3-}}$ concentration in the supernatant in the absence of the inhibitor, and $[\mathrm{PO_4^{3-}}]_i$ is the initial $\mathrm{PO_4^{3-}}$ concentration at the beginning of the experiment. For the second method, the initial $\mathrm{Ca^{2+}}$ concentration of the experimental solution was 1,500 mg/L. The solution was prepared with anhydrous calcium chloride, anhydrous sodium bicarbonate, dihydrogen phosphate, and secondary-treated municipal wastewater, and its initial $\mathrm{PO_4^{3-}}$ concentration, initial $\mathrm{HCO_3^-}$ concentration and pH value were 5, 200 mg/L and 8.0 ± 0.1, respectively. The initial concentrations of $\mathrm{Ca^{2+}}$ and $\mathrm{HCO_3^-}$ of the experimental solution were as much as that of the highly concentrated recirculating cooling water when applying the pH-controlled process. The following experiment procedure was the same as the first method mentioned above.

2.3.2. Zinc salts scale inhibition

The zinc salts scale (zinc carbonate, zinc hydroxide, etc.) inhibition performance of the dispersants was tested at the initial $\mathrm{Ca^{2+}}$ concentration of 1,500 mg/L [28]. The experimental solution was prepared with zinc sulfate heptahydrate, anhydrous calcium chloride, anhydrous sodium bicarbonate and the secondary-treated municipal wastewater at an initial $\mathrm{Zn^{2+}}$ concentration of 5 mg/L and an initial $\mathrm{HCO_3^-}$ concentration of 200 mg/L, which was buffered by sodium bicarbonate at various pH ranges. A dispersant was added into the solution which was metered in a volumetric flask of 500 mL, and the pH of the solution was adjusted to a predetermined value by adding sodium borate solution. The flask then was put into the constant temperature water bath at a constant temperature of 80℃ for 10 h. After the flask was cooled to room temperature, the residual $\mathrm{Zn^{2+}}$ concentration of the supernatant was analyzed by EDTA titration [27].

2.3.3. Corrosion inhibition

The corrosion inhibition performance of the cooling water treatment chemical program was tested at the initial $\mathrm{Ca^{2+}}$ concentration of 1,500 mg/L [28,29]. The experimental solution was prepared with anhydrous calcium chloride, anhydrous sodium bicarbonate, and the secondary-treated municipal wastewater, and then the corrosion and scale inhibitors and dispersants were all added into the solution. The pretreated and weighed $20^{\#}$ carbon steel coupons were fixed on a RCC-II rotating coupon corrosion tester (Jiangsu Gaoyou Instrument Factory, China) and dipped into the experimental solution. The rotating coupon experiment was performed for 72 h at the constant temperature of 45℃ and the rotating speed of 75 r/min. The coupons were post-treated and weighed, and the corrosion rate was calculated by the weight loss of the coupons from the following equation:

$$\text{Corrosion rate (mm/a)} = \frac{87,600 \times \Delta W}{S \times \rho \times t} \tag{2}$$

where ΔW is the weight loss of the coupon (g), S is the superficial area of the coupon ($\mathrm{cm^2}$), ρ is the density of the coupon ($\mathrm{g/cm^3}$), and t is the experimental time (h). In the present study, the corrosion rate is represented by a depth of metal in a period of time, and its unit is millimeters per year.

2.4. Pilot-scale RCWS experiment

A pilot-scale RCWS designed and installed by ourselves was used to confirm the performance of the cooling water chemical program [28,30], and its process is shown in Fig. 1.

The whole process can be described as: first, the cooling water was pumped from the cooling tower basin to the test tube ($20^{\#}$ carbon steel, Ø10 × 1 × 500 mm, chromium plated outside) in the heat exchanger and its flow rate was controlled at 180 L/min by a rotameter. Then, the cooling water was heated by the water vapor generated in the heat exchanger and the inlet and outlet temperatures of the tube were maintained at 32.0 ± 1.0℃ and 42.0 ± 1.0℃, respectively. Next, the heated water entered the upper part of the cooling tower and was distributed into droplets by nozzles. After that, the water passed fillers for exchanging heat with the air which was blown from the lower part of the cooling tower by a Root's blower. Finally, the cooled water went down into the cooling tower basin and finished the circuit.

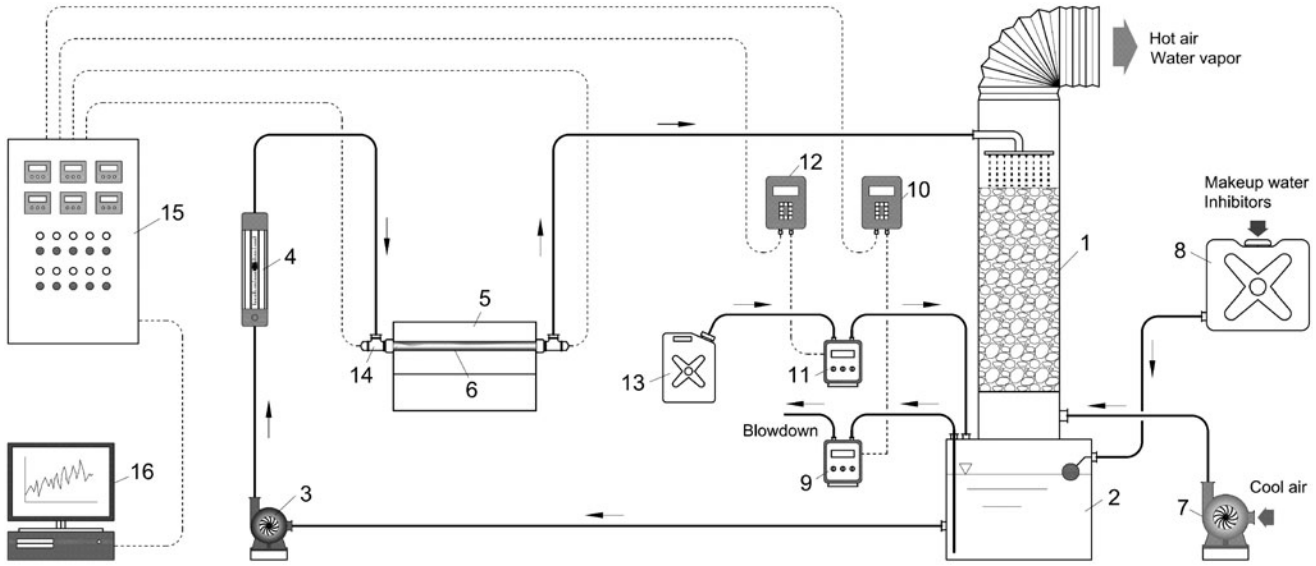

Fig. 1. The process diagram of the pilot-scale RCWS. (1) Cooling tower; (2) cooling tower basin; (3) circulating pump; (4) rotameter; (5) heat exchanger; (6) test tube; (7) root's blower; (8) make-up water tank; (9) blowdown pump; (10) conductivity controller; (11) acid-dosing pump; (12) pH-controller; (13) sulfuric acid tank; (14) temperature probe; (15) control cabinet; (16) computer.

The secondary-treated municipal wastewater detailed in Section 2.1 was used as the make-up for the system in the experiment. The water volume of the whole system was balanced by adding make-up water to the cooling tower basin through a ball float valve. The corrosion and scale inhibitors were mainly dosed along with the make-up water. If the content of the corrosion and scale inhibitors in the water was lower than the predetermined values, extra dosages of the inhibitors would be supplemented to the cooling tower basin directly. Moreover, SDIC of 30 mg/L was added to the cooling tower basin everyday for eliminating the biofouling. The cooling water would be automatically discharged from the cooling tower basin when the Ca^{2+} concentration exceeded 1,500 mg/L [31,32]. The pH of the cooling water was managed in a scheduled range during the test by an automatic pH-controller [32]. The test lasted for 20 d, and the adhesion rate and the corrosion rate of the test tubes were obtained by the weight gain and the weight loss of the tubes. The adhesion rate was calculated using the following equation:

$$\text{Adhesion rate (mcm)} = \frac{720{,}000 \times (W_1 - W_2)}{S \times t} \tag{3}$$

where W_1 is the weight of the test tube without cleansing by acid after the experiment (g), W_2 is the weight of the post-treated test tube after the experiment (g), S is the inner superficial area of the test tuber (cm^2), and t is the experimental time (h). The adhesion rate is represented by a weight of total deposit on an inside surface of test tube in a period of time, and the unit of mcm is an abbreviation of mg/(cm^2 month). At the same time, some coupons of $20^{\#}$ carbon steel were suspended into the cooling tower basin to get comparable data for the corrosion rate.

3. Results and discussion

3.1. The calcium phosphate scale inhibition performance

Generally, the chemical program used to treat recirculating cooling water mainly includes three kinds of ingredients—scale inhibitors, corrosion inhibitors, and dispersants [21]. Dispersants, on one hand, can disperse the tiny crystals of scales and colloids; on the other hand, they can inhibit the formation of calcium phosphate scale and zinc salts scale. In this research, due to the high phosphate content in the secondary-treated municipal wastewater, calcium phosphate scale will be easily formed when the wastewater is concentrated in the RCWS. As a corrosion inhibitor, PO_4^{3-} cannot perform corrosion inhibition once it precipitates as scales. So a dispersant with better calcium phosphate scale inhibition performance is desired to ensure there is enough soluble phosphate in the cooling water for corrosion inhibition even if the make-up water is concentrated to five times. The calcium phosphate scale inhibition performances of four copolymer dispersants, thus, were evaluated in the present study. Fig. 2 shows that the calcium phosphate scale inhibition efficiencies of the four dispersants all went up with the increase of their dosages, but the minimum dosages to obtain the highest efficiencies were different. The calcium phosphate scale inhibition efficiencies of LH-304, ZF322(A)MS, and JC-3211 reached over 90% at their dosages of 4 mg/L, but LN-104B did not get the satisfactory scale inhibition efficiency until its dosage increased to 6 mg/L. Actually, the four dispersants did not show significant distinction of calcium phosphate scale inhibition performance at the initial Ca^{2+} concentration of 250 mg/L. Therefore, a further test was conducted to evaluate the calcium phosphate scale inhibition efficiency in a condition which simulated the highly concentrated RCWS using secondary-treated municipal wastewater as the make-up. As shown in Fig. 3, the calcium phosphate scale inhibition efficiencies of ZF322(A)MS and JC-3211 were not satisfactory under the condition of highly concentrated RCWS, and they declined with the increase of initial PO_4^{3-} concentration. This declination could not be improved even if the dosages of these two dispersants rose to 14 mg/L. In contrast, the calcium phosphate scale inhibition efficiencies of LH-304 and LN-104B were very good. Despite the scale inhibition efficiencies decreasing with the growth of the initial PO_4^{3-} concentration, it would be enhanced by increasing the dosages of these two dispersants. For LH-304 and LN-104B, little deposit of calcium phosphate in the experimental solutions was observed when a proper ratio of the initial PO_4^{3-} concentration to the dosage of dispersants was applied. Since the calcium phosphate scale inhibition performance of LN-104B was relatively better than that of LH-304, the dispersant of LN-104B was chosen to be one of the ingredients of the recirculating cooling water treatment chemical program.

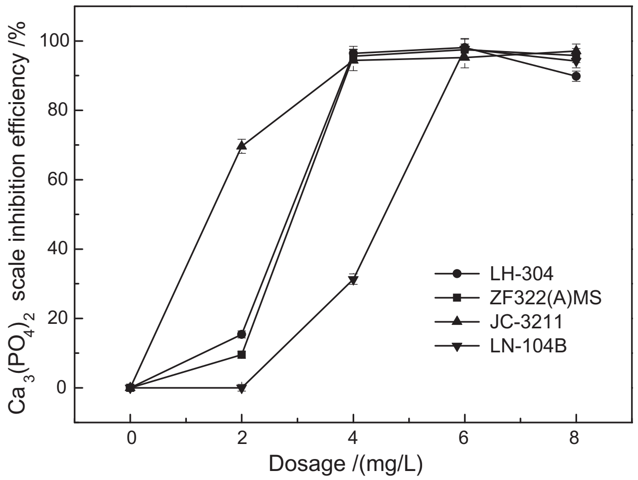

Fig. 2. The calcium phosphate scale inhibition performances comparison at an initial Ca^{2+} concentration of 250 mg/L. Experimental condition: $[PO_4^{3-}] = 5$ mg/L; pH 9.1 ± 0.1.

3.2. The zinc salts scale inhibition performance

Zn^{2+} is usually used as a corrosion inhibition additive in recirculating cooling water treatment, and the combination of PO_4^{3-} and Zn^{2+} can bring about very good corrosion inhibition [33]. But Zn^{2+} also readily scales out as zinc salts when the water is alkaline, and PO_4^{3-} cannot result in acceptable corrosion inhibition alone. Normally, the dispersant can also inhibit the formation of zinc salts scale. For that reason, the zinc salts scale inhibition performances of the four dispersants mentioned above were also tested in this investigation. Two pH ranges were chosen in this experiment for understanding the influence of pH value on the precipitation of zinc salts scale better, since the compounds of zinc changes very much under an alkalescence condition. Fig. 4 shows that the pH of the experimental solution has a significant effect on the formation of zinc salts scale. Little Zn^{2+} scaled out in the solution in the absence of dispersants (control experiment) at the pH range of 7.8–7.9. However, the residual Zn^{2+} concentration of the solution dropped to below 1 mg/L at the pH range of 8.2–8.4. It indicates that the pH is more important than the dispersants in terms of zinc salts scale inhibition. The residual Zn^{2+} concentrations were varied in the experiments in the presence of dispersants under the condition of higher pH. It is clear that LH-304 and LN-104B have much better zinc salts scale inhibition performance than the other two dispersants.

3.3. The boundary condition of the PO_4^{3-} *concentration*

According to our observation, the phosphate content in the secondary-treated municipal wastewater fluctuated from time to time (Table 1). Sometimes, it was so low that it could not meet the need of corrosion inhibition even after being concentrated in the RCWS. In order to find out the minimum PO_4^{3-} concentration that the corrosion inhibition standard required [20], the effects of PO_4^{3-} concentration on the corrosion inhibition were investigated. LN-104B and PESA [34] were dosed as the dispersant and the scale inhibitor and their dosages were 10 and 6 mg/L, respectively. Two pH ranges were chosen in this experiment for making it clear the effect of pH value

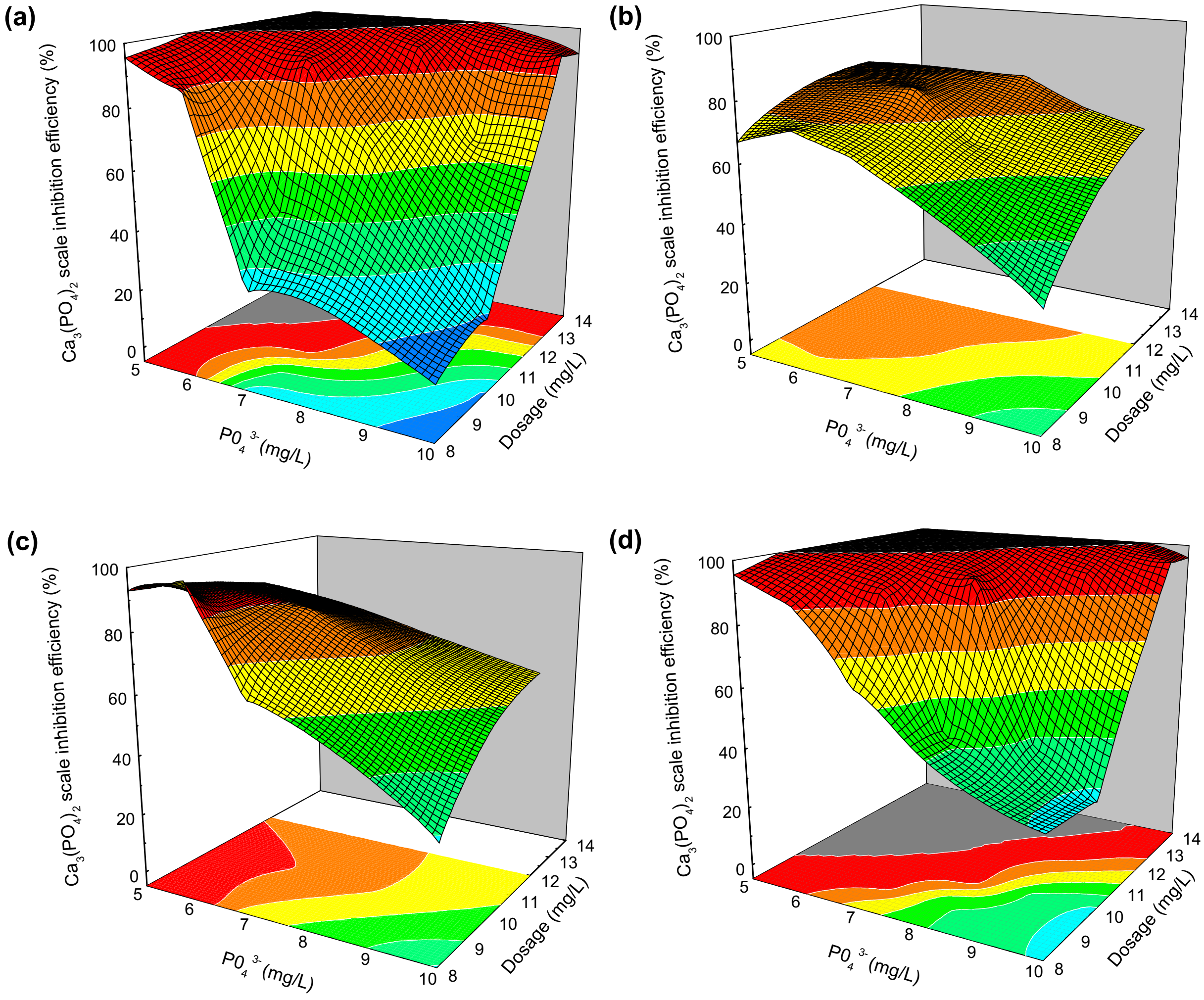

Fig. 3. The calcium phosphate scale inhibition performances comparison at a high initial Ca^{2+} concentration of 1,500 mg/L. (a) LH-304; (b) ZF322(A)MS; (c) JC-3211; (d) LN-104B. Experimental condition: $[PO_4^{3-}] = 5$ mg/L; $[HCO_3^-] = 200$ mg/L; pH 8.0 ± 0.1.

on the direct corrosion and the indirect corrosion due to the change of PO_4^{3-} and Zn^{2+} concentrations. As shown in Fig. 5, the pH value and the Zn^{2+} concentration both affected the minimum PO_4^{3-} level. The corrosion rate was higher than 2.0 mm/a at the pH range of 7.4–7.6 and the Zn^{2+} concentration of 1 mg/L, even if the PO_4^{3-} concentration of the experimental solution was up to 6 mg/L. At the same pH range, the corrosion rate however fell gradually at the Zn^{2+} concentration of 2 mg/L with the growth of the PO_4^{3-} concentration, and good corrosion inhibition could be achieved at the PO_4^{3-} concentration of 5 mg/L. Moreover, the corrosion inhibition was significantly improved at the pH range of 7.9–8.1, and the requirement of below 0.075 mm/a could be met at the Zn^{2+} concentration of 1 mg/L and the PO_4^{3-} concentration of 3.5 mg/L. To summarize, in the general pH value range of pH-controlled RCWSs, the corrosion rate could be well controlled at the PO_4^{3-} concentration of 5 mg/L and the Zn^{2+} concentration of 2 mg/L.

3.4. The optimization of the chemical program

Based on the experimental results in Section 3.3, the corrosion inhibition was difficult to guarantee if the PO_4^{3-} concentration was below 5 mg/L. Therefore, a method of adding an organic phosphate inhibitor [35]—HEDP, was developed to ensure that there were enough corrosion inhibitors in the RCWS. In the present study, the total phosphate content in the experimental solution was maintained to 5 mg/L at the Ca^{2+} of 1,500 mg/L and the Zn^{2+} concentration of 2 mg/L.

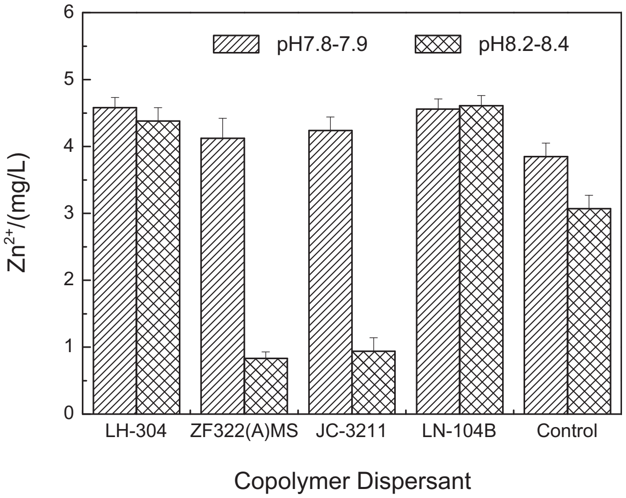

Fig. 4. The zinc salts scale inhibition performance comparison at a high initial Ca^{2+} concentration of 1,500 mg/L under the condition of different pH values. Experimental condition: $[Zn^{2+}] = 5$ mg/L; $[HCO_3^-] = 200$ mg/L.

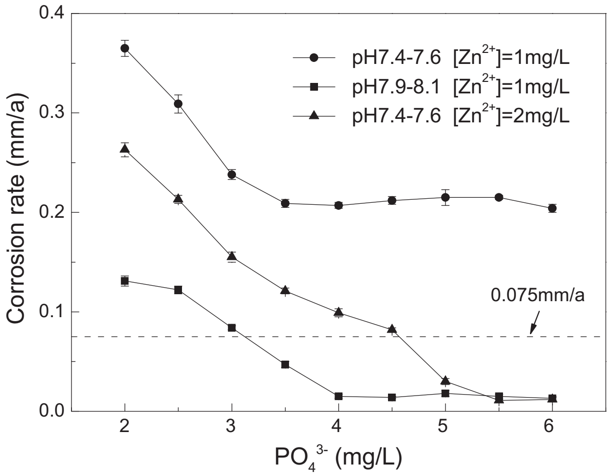

Fig. 5. The Effect of PO_4^{3-} concentration on the corrosion rate. Experimental condition: $[Ca^{2+}] = 1{,}500$ mg/L.

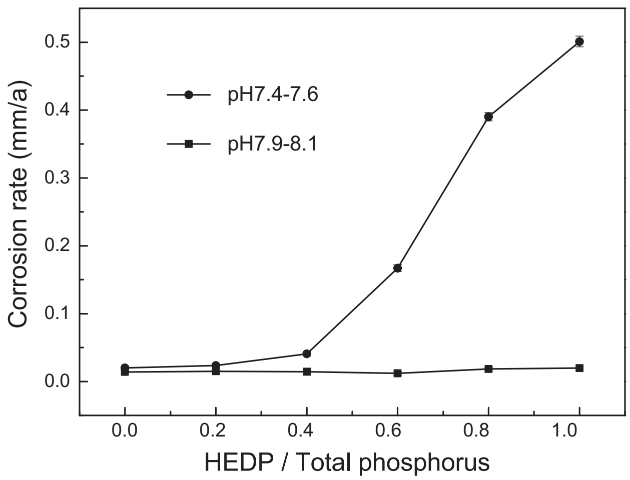

Fig. 6. The effect of HEDP/total phosphate on the corrosion rate. Experimental condition: $[Ca^{2+}] = 1{,}500$ mg/L.

Fig. 6 exhibits that a good corrosion inhibition could be achieved at the pH range of 7.9–8.1 regardless of the proportion of HEDP in the total phosphate. In contrast, the corrosion rate went up with the proportion increase of HEDP at the pH range of 7.4–7.6. Notably, the corrosion rate skyrocketed at the proportion of HEDP of up to 0.6. In conclusion, it is very important to control the pH value of the highly concentrated RCWS, and satisfactory corrosion inhibition will be guaranteed in the higher pH range (7.9–8.1) by the combination of PO_4^{3-} and HEDP. If the pH value drops to below 7.6, the PO_4^{3-} concentration must be more than 3 mg/L even if HEDP is dosed. So far, an optimized cooling water treatment chemical program was developed for highly concentrated RCWS made up by secondary-treated municipal wastewater. We named it RWP-1. It includes: (1) the corrosion inhibitors of phosphate and HEDP whose summed dosage is 5 mg/L; (2) the scale inhibitor of PESA whose dosage is 6 mg/L; (3) the dispersant of LN-104B whose dosage is changeable according to the PO_4^{3-} concentration of the cooling water; and (4) the synergistic corrosion additive of zinc sulfate heptahydrate whose dosage (calculated by Zn^{2+}) is 2 mg/L.

3.5. *Pilot-scale experiment verification*

A pilot-scale experiment was conducted to verify the performance of the cooling water treatment chemical program (RWP-1) which was developed from the bench experiments. As shown in Fig. 7(a), the Ca^{2+} concentration increased gradually in the first five days of the experiment because the cooling water was heated and concentrated in the pilot-scale RCWS. At the same time, the cycle of concentration exhibited the same trend, growing with the Ca^{2+} concentration; until the Ca^{2+} concentration reached 1,500 mg/L and the cycle of concentration approached 6.0, when the RCWS started to blow down. After that, the Ca^{2+} concentration and the cycle of concentration both leveled off. In contrast, the total alkalinity went up a little to the highest point of 300 mg/L at first, and then it decreased by dosing sulfuric acid to the RCWS for inhibiting the formation of calcium carbonate scale. The total alkalinity went down in the following three days until its concentration was stabilized at about

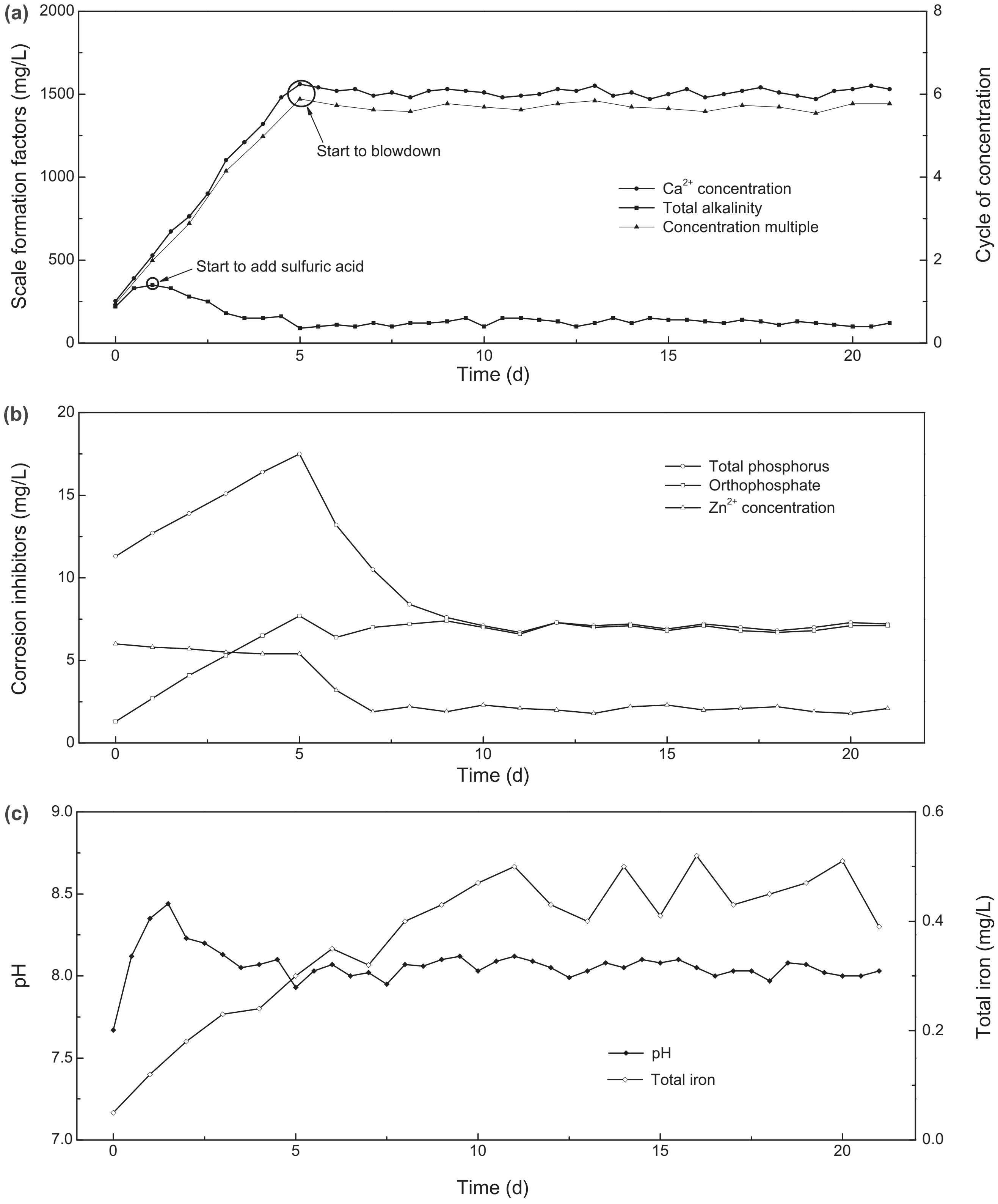

Fig. 7. The variation of cooling water characteristics in the pilot-scale experiment. (a) Ca^{2+} concentration, total alkalinity and cycle of concentration vs. time; (b) total phosphorus, orthophosphate and Zn^{2+} concentration vs. time; (c) pH value and total iron vs. time.

Table 2
Pilot-scale experimental results and the comparison with the data from some other researches on highly concentrated recirculating cooling water treatment

No.	Water treatment chemical program	Scale	Ca^{2+} (mg/L)	Cycle of concentration	Corrosion rate (mm/a) Test tube	Corrosion rate (mm/a) Coupon	Adhesion rate (mcm)	Refs.
1	RWP-1	Pilot	≈1,600	5.5–6.0	0.023	0.015	2.32	/
2	TS-225D	Pilot	<130	7.0–8.0	0.024	0.009	10.4	[16]
3	HZ-3	Pilot	<350	3.0–4.0	0.029	0.014	5.42	[17]
4	YSW105	Pilot	≈1,600	≈4.5	0.045	0.021	4.13	[18]
5	RP-04(QL)	Plant	<550	5.0–6.0	0.019	/	5.15	[19]
6	YSW105	Plant	<1,300	≈4.0	0.030	0.009	5.90	[18]
7	RP-12(MM)	Plant	<400	4.5–5.5	0.024	/	8.45	[5]

150 mg/L. From the Ca^{2+} concentration of the make-up water and the cooling water and the cycle of concentration, it is easily known that little calcium scale (calcium carbonate, calcium phosphate, etc.) precipitated in the system. Fig. 7(b) shows the amount of the corrosion inhibitors in the cooling water. At the beginning of the experiment, HEDP was added into the cooling water and made the content of the phosphorous corrosion inhibitors up to 11 mg/L in order to mitigate the initial corrosion which usually occurs on a surface of clean metal. Additionally, zinc sulfate heptahydrate of 6 mg/L was dosed to speed up the formation of the corrosion inhibition film on the inner wall of the test tubes. Along with the cooling water concentrating, the total phosphorus content and the orthophosphate content both went up, but not in direct proportion to the cycle of concentration, and the Zn^{2+} concentration decreased a little instead. It indicates that a corrosion inhibition film was developed in this RCWS by the combination of PO_4^{3-}, HEDP, and Zn^{2+}. After blowdown, the total phosphorus content and the Zn^{2+} concentration both decreased until their amount was around 7.5 and 2.3 mg/L, respectively. A little higher content than that of the optimized cooling water treatment chemical program was used in the experiment for making it sure to get satisfactory corrosion inhibition. The content of the corrosion inhibitors leveled off in the following days, and no more HEDP was dosed as the phosphate in the make-up water (secondary-treated municipal wastewater) is adequate for the corrosion inhibition. Therefore, the cost for the corrosion inhibitors is expected to be substantially saved, and the environmental risk of the excess emission of phosphate will be reduced. In Fig. 7(c), the variation trend of pH value was as same as that of total alkalinity in Fig. 7(a). The pH value in the steady operation stage was 7.8–8.2 which effectively balanced the scale inhibition and the corrosion inhibition. The total iron content increased in first 10 days because the iron ions in the make-up water were concentrated and the initial corrosion occurred in the RCWS. After the formation of the corrosion inhibition film, the corrosion was well controlled and the total iron content did not grow any more. In the period of the pilot-scale experiment, the total iron content of the cooling water was below 0.6 mg/L, which also satisfies the standard limit of recirculating cooling water treatment. The pilot-scale experimental results are shown in Table 2. The corrosion rate and the adhesion rate of the test tubes are 0.023 mm/a and 2.32 mcm, respectively, which both meet the requirements of the recirculating cooling water treatment (the adhesion rate needs to be below 15 mcm) [20]. Table 2 also lists some data from other research on highly concentrated recirculating cooling water treatment for comparison. The chemical programs were validated in the pilot-scale units and the actual plants. For TS-225D program, the cycle of concentration was up to 8.0 simply because a fresh water with low calcium hardness (the Ca^{2+} concentration is below 20 mg/L) and low alkalinity was used as the make-up. A natural pH process was applied in this RCWS, which was known to easily operate and well controlled when the sum of calcium hardness and total alkalinity is not more than 900 mg/L. In terms of HZ-3 and RP-04(QL) programs, the make-up waters were both medium calcium hardness (the Ca^{2+} concentration is around 80 mg/L) fresh water, and pH-controlled processes were applied in these two RCWSs. By dosing sulfuric acid, it was not difficult to raise the cycle of concentration to 6.0. In contrast, YSW105 program was developed for a RCWS which used extremely high calcium hardness (the

Ca^{2+} concentration is around 350 mg/L) fresh water as make-up and operated under the condition of high Ca^{2+} concentration (up to 1,300 mg/L). It has been verified to be a significantly effective pH-controlled process, and a great amount of fresh water has been saved by using it. Being different from the aforementioned programs, RP-12(MM) program was used in a RCWS whose make-up was wastewater. But the Ca^{2+} concentration of the system needed to be maintained below 300 mg/L in order to meet the requirement of the recirculating cooling water treatment. Apparently, RWP-1 program is suitable for a highly concentrated RCWS which used high hardness secondary-treated municipal wastewater as make-up, and more fresh water resources will be conserved this way than applying the other chemical programs mentioned above.

4. Conclusion

The phosphate in the secondary-treated municipal wastewater can be comprehensively utilized as a corrosion inhibitor when the wastewater is reused in the RCWS. With the aid of Zn^{2+}, HEDP, and a copolymer dispersant of LN-104B, satisfactory corrosion inhibition was achieved. LN-104B has an excellent capability to mitigate the precipitation of calcium phosphate scale and zinc salts scale which has been verified by the bench experiments. The calcium phosphate scale inhibition efficiency of LN-104B was up to 94% and the residual Zn^{2+} concentration was over 4.5 mg/L at the Ca^{2+} concentration of 1,500 mg/L, the PO_4^{3-} concentration of 10 mg/L and the Zn^{2+} concentration of 5 mg/L, respectively. A chemical program – RWP-1 was developed and it includes: (1) corrosion inhibitors of phosphate and HEDP whose summed dosage is 5 mg/L; (2) a scale inhibitor of PESA whose dosage is 6 mg/L; (3) a dispersant of LN-104B whose dosage is changeable according to the PO_4^{3-} concentration of the cooling water; and (4) a synergistic corrosion inhibitor of zinc sulfate heptahydrate whose dosage is 2 mg/L. RWP-1 program is appropriate for a highly concentrated RCWS which uses high hardness secondary-treated municipal wastewater as make-up, and the corrosion rate and the adhesion rate in the pilot-scale experiment are only 0.023 mm/a and 2.32 mcm, respectively, which both meet the requirements of the recirculating cooling water treatment. As a result, the comprehensive utilization of the phosphate in the wastewater will reduce the consumption of corrosion inhibitors and cut down the operating costs of RCWS. In addition, great amounts of fresh water and phosphorus resources are expected to be conserved.

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