

Effect of optimized three-component antiscalant mixture on calcium carbonate scale deposition

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ABSTRACT

The mixture of 1-hydroxyethane-1,1-diphosphonic acid (HEDP), and polyacrylic acid (PAA) and synthesized hydrolyzed polymaleic anhydride (HPMA) was optimized by using simplex lattice of Design-Expert software through calcium carbonate precipitation method. The optimum mass ratio of HEDP, PAA and synthesized HPMA was obtained at 10/10/80, which showed excellent performance on controlling calcium carbonate deposition. The antiscaling efficiency of the optimum mixture was 84% and 95%, respectively, in the calcium carbonate precipitation test and the calcium carbonate scale deposit test. The optimum mixture could disturb the crystal growth of calcium carbonate and then affect the morphology and crystal structure of the calcium carbonate precipitates.

Key words | antiscalant, calcium carbonate, cooling water system, simplex-lattice design, synergistic effect

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INTRODUCTION

Water used in the cooling water systems usually contains particles, organic matters and scale-forming ions containing Ca^{2+} , Mg^{2+} , CO_3^{2-} , SO_4^{2-} and HCO_3^- . The constituents could be concentrated many times because of the evaporative loss of water. The elevated concentration and high water temperature could cause severe mineral deposition and adhesion onto the heat transfer equipment surfaces (mineral scaling), along with the problems of corrosion (Shen *et al.* 2013; Wei *et al.* 2016) and biofouling (Wang *et al.* 2013). It is well known that calcium carbonate, in particular, is the predominant mineral scale compound in cooling water systems (Zhao *et al.* 2014). The problem of scaling in cooling water systems during recirculation poses great challenges from both economical and technical points of view, decreasing system efficiency and increasing frequency of chemical cleaning.

To mitigate the problem of mineral scaling, chemicals and antiscalants including but not limited to polyacrylic acid (PAA), polyacrylamide, hydrolyzed polymaleic anhydride (HPMA), 1-hydroxyethane-1,1-diphosphonic acid (HEDP) and polyphosphates were widely used (Al-Roomi *et al.* 2015; Chen *et al.* 2015; Liu *et al.* 2015; Mithil Kumar *et al.* 2015; Asghari *et al.* 2016; Bu *et al.* 2016; Wang *et al.* 2016). These antiscaling chemicals control mineral scale through mainly two antiscaling mechanisms: one is that

antiscalants could keep more scale-forming positive ions (e.g. Ca^{2+} and Mg^{2+}) in the solution from being precipitated through complexation action (Eriksson *et al.* 2007); the other is that the antiscaling chemicals could interact with mineral nuclei to disrupt the crystallization process and keep the crystal particles dispersed in the aqueous suspension, rendering them less prone to sedimentation or adhesion onto the equipment surfaces (Shakkthivel & Vasudevan 2006; Eriksson *et al.* 2007). HEDP, HPMA and PAA have been widely used as scale inhibitors, corrosion inhibitors or dispersants. PAA has the 'threshold effect' of CaCO_3 inhibition which could absorb the growing crystal phases of the nuclei and prevent vaterite transforming to aragonite or calcite, which results in the distortion and retardation of the crystal growth (Tang *et al.* 2008; Kavitha *et al.* 2011). HEDP could modify the structure of calcium carbonate by incorporating into the crystals and thus decrease scale formation on the heat exchanger surfaces (Marín-Cruz *et al.* 2006). A. Martinod *et al.* investigated the effect of HPMA on the growth of calcium carbonate particles in the micrometer size range on stainless steel surface, HPMA could affect the growth of CaCO_3 crystals due to adsorption of carboxylate ions on the nuclei of calcium carbonate (Martinod *et al.* 2008). In addition, we synthesized HPMA and investigated the effect of the synthesized

HPMA on the morphologies and crystal structures of calcium carbonate precipitates in our previous work (Shen *et al.* 2012). Mixtures of different kinds of scale inhibitor according to a certain mixing ratio may have much higher scale inhibition efficiency. Experiments and optimization are usually necessary to find a good mixing ratio. Reports on the optimization of the mixture of HEDP, PAA and HPMA were not easy to find. And the synergetic effect of HEDP, HPMA and PAA on the crystal of calcium carbonate is still lacking.

In the present study, the mixture of HEDP, PAA and synthesized HPMA was optimized by using simplex lattice mixture design according to the Design-Expert software, based on calcium carbonate precipitation method. The morphologies and crystal structures of precipitates and deposits were investigated using scanning electron microscope (SEM) and X-ray diffraction (XRD). The synergetic effect of HEDP, HPMA and PAA on the crystal of calcium carbonate was discussed.

METHODS

Chemicals and reagents

Chemicals are analytical reagents which were used as received from commercial suppliers without further purification, unless otherwise specified. HEDP and PAA were bought from Nanjing Naco Water Treatment Technology Co, Ltd.

Synthesis of HPMA

The synthesis process of HPMA was discussed in our previous work in detail (Shen *et al.* 2012).

Optimization of the three-component antiscalant mixture

The inhibition ability of the mixture of HEDP, PAA and synthesized HPMA was optimized by using simplex lattice of Design-Expert software (Stat-Ease, Inc.) under the condition of calcium carbonate precipitation test. The experimental design was carried out with some constraints (Table 1, A, B and C is for HEDP, HPMA and PAA, respectively). A special cubic mixture model was used to describe the relationship between the inhibition efficiency and the components (Gorman & Hinman 1962).

Table 1 | Constraints of simplex lattice design

Low \leq	Constraint	\leq High
0.1 \leq	A	≤ 0.8
0.1 \leq	B	≤ 0.8
0.1 \leq	C	≤ 0.8
	A + B + C	=1.0

Evaluation of antiscalant

There are two methods to evaluate antiscalants in the present study. One is calcium carbonate precipitation test using ethylenediaminetetraacetic acid (EDTA) titration under static condition. The other is calcium carbonate deposits weighing test through weighing the stainless steel specimen after mineral scaling test under stirring condition.

Calcium carbonate precipitation test

The calcium carbonate precipitation test was designed to provide a quantitative measure of the abilities of scale inhibitors to prevent the precipitation of Ca^{2+} from bulk solution. The initial concentration of Ca^{2+} was 240 mg/L in the calcium carbonate precipitation test. The details were described in our previous work in detail (Shen *et al.* 2012).

The precipitates in the test were carefully collected and dried in room temperature for morphology and crystal structure analysis. The XRD pattern was recorded on a Bruker D8 Advance XRD instrument (Cu, $K\alpha$), the diffraction angle (2θ) in the range of 20–80° was scanned (Bruker, Germany). SEM images were obtained using JEOL JSM-6380LV electron microscope (JEOL JSM-6380LV, Japan).

Calcium carbonate scale deposit weighing test

The calcium carbonate scale deposit weighing test was carried out in a 500 mL five mouth flask. To avoid the evaporation of the solution, the 40 cm long glass tube ($\Phi = 3$ mm) plugged by the rubber stopper was used as a reflux condenser. The prepared 304 stainless steel specimen was fixed in the flask after being weighed. Three parallel specimens were used for one test. The flasks were placed in a water-bath at 80 °C constantly for 24 h. During the test, the agitation speed was kept at 200 r/min so that the liquid velocity on the specimen surface was almost 0.6 m/s. The stainless steel specimens were carefully removed and placed in a drier at room temperature without disturbing the deposits on the surface. The specimen was measured

using analytical balance (Mettler AE163). Final weighing was performed only after a constant mass was achieved (mass measurement variation <0.05 mg/h). Three parallel specimens were measured and the average value was reported as the mineral mass on the specimen. The mass of deposits on the test specimen was calculated based on the specimen mass before and after the test. The scale inhibition efficiency for scale deposits was calculated as: $\eta_s = (m_0 - m_1)/m_0 \times 100\%$, where m_1 is the mass of deposits on the specimen surface during scaling test with adding antiscalant; m_0 is the mass of deposits on the specimen surface during scaling test for the control sample and η_s is the antiscalant efficiency of the calcium carbonate scale deposit test.

Following the weighing test, the stainless steel specimens were carefully collected in a drier for morphology analysis of the calcium carbonate scale deposit. SEM images were obtained using JEOL JSM-6380LV electron microscope (JEOL JSM-6380LV, Japan).

RESULTS AND DISCUSSION

Optimization of 3-component antiscalant mixture

According to Design-Expert software, the mixture of HEDP, PAA and the synthesized HPMA was optimized using simplex lattice design with design constraints. The model F-value of 24.05 and P-value of 0.0124 implied that the special cubic mixture model was significant. There was only a 1.24% chance that a 'Model F-Value' this large could occur due to noise. The final equation of the special cubic mixture model in terms of actual components was shown in Equation (1), where A, B and C is for HEDP, HPMA and PAA, respectively. E is the antiscalant efficiency in the calcium carbonate precipitation test.

$$E = 71.9 \times A + 86.3 \times B + 72.9 \times C - 26.2 \times A \times B - 26.3 \times A \times C - 28.9 \times B \times C + 223.7 \times A \times B \times C \quad (1)$$

Based on the equation of the special cubic mixture model, the relationship between the predicted value and actual value was obtained and is shown in Figure 1. The actual value was evenly distributed beside the predicted line, which indicated that the special cubic mixture model was significant.

The 3D surface model graph of the three-component antiscalant mixture was calculated based on the special

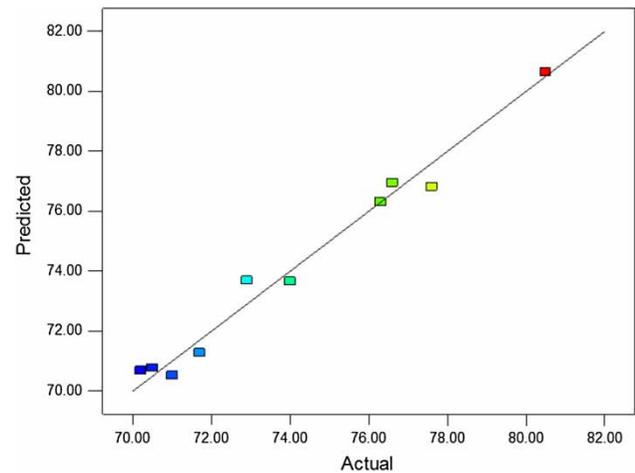


Figure 1 | The predicted value (—) vs. actual value (□).

cubic mixture model, and shown in Figure 2. It was clearly seen that the antiscalant efficiency showed a marked increase when the proportion of the synthesized HPMA was raised from 10% to 80%. The mixture of HEDP, PAA and synthesized HPMA showed much higher antiscalant efficiency at the mass ratio of 10/10/80, which was the optimum three-component antiscalant mixture.

Calcium carbonate precipitation test

The calcium carbonate precipitation test was carried out through EDTA titration of Ca^{2+} content in the simulating aqueous solution, which could quickly reflect the performance of scale inhibitor on Ca^{2+} . After 24 h precipitation at 80°C under static condition, the concentration of Ca^{2+}

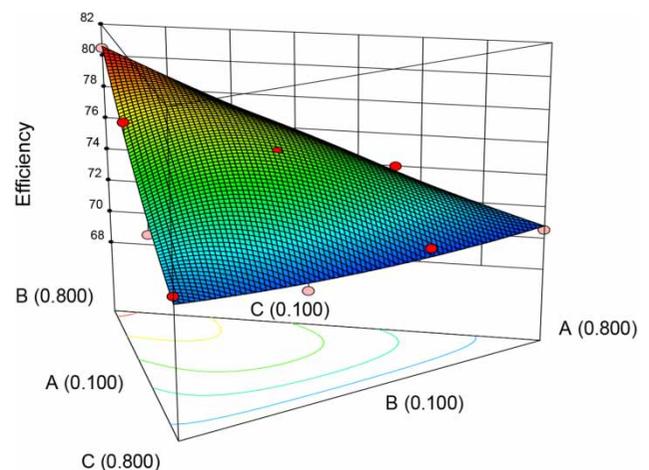


Figure 2 | 3D surface model graph of the three-component mixture: A, B and C are for HEDP, HPMA and PAA.

was quantified through EDTA titration. The antiscalant efficiency was calculated based on the titration results of both blank samples and scale inhibitor samples. The synthesized HPMA and the optimum three-component antiscalant mixture of HEDP, PAA and the synthesized HPMA were evaluated under the calcium carbonate precipitation test. The results are shown in Figure 3.

The antiscalant efficiency of the synthesized HPMA increased from 52% to 71% when concentration increased from 2 mg/L to 6 mg/L, and then increased slowly to 78% when the concentration increased to 30 mg/L. In the presence of HPMA, Ca^{2+} could adsorb onto the main chain of HPMA molecular through chelate reaction (Eriksson *et al.* 2007). The formation of soluble complexes of HPMA- Ca^{2+} through carboxylic acid groups increased the concentration of Ca^{2+} in the bulk solution and, thereby, decreased the rate of calcium carbonate precipitation (Lin *et al.* 2005). Otherwise, HPMA may adsorb onto the active sites of the crystal nucleus, thereby disturbing the growth of the crystal of calcium carbonate.

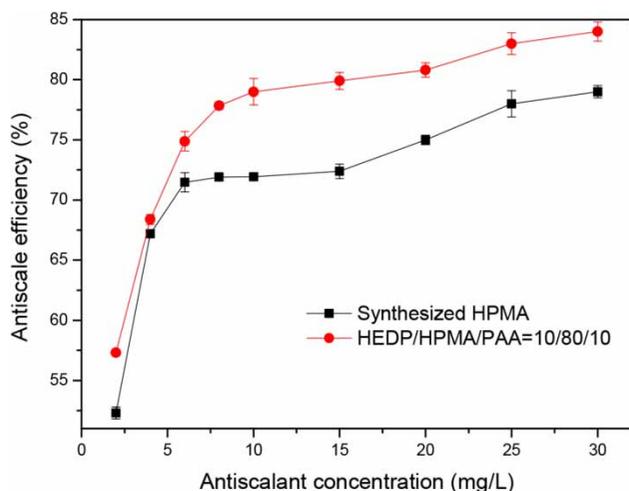


Figure 3 | The antiscalant efficiency of calcium carbonate precipitation test.

The optimum mixture of HEDP, PAA and synthesized HPMA at the mass ratio of HEDP/HPMA/PAA = 10/80/10 showed much higher efficiency than HPMA. The antiscalant efficiency of the mixture showed similar trend to HPMA. The antiscalant efficiency of the optimum mixture increased from 57% to 80% when the concentration increased from 2 mg/L to 10 mg/L, and then increased slowly to 84% when the concentration increased to 30 mg/L. HEDP and PAA enhanced the effect of the synthesized HPMA on Ca^{2+} . Both the synthesized HPMA and the optimum three-component antiscalant mixture showed ‘threshold’ effect under the condition of the calcium carbonate precipitation test. Even less than 10 mg/L, the synthesized HPMA and the optimum mixture provided excellent antiscalant efficiency. And the efficiency increased insignificantly when the concentration increased from 10 mg/L to 30 mg/L.

The precipitates formed in the calcium carbonate precipitation test in the presence of antiscalant (10 mg/L) were collected for morphology analysis by using SEM. The SEM images are shown in Figure 4.

The two occurring mineral phases, vaterite and calcite, could clearly be distinguished by their characteristic morphologies. Vaterite could be recognized as framboid spherical shape (Nehrke & Van Cappellen 2006) while calcite as rhombohedra crystallites (Weiner *et al.* 2005). Figure 4(a) shows regular shaped rhombohedra in the absence of antiscalant corresponding to calcite phase. However, the regular shaped rhombohedrons disappeared in the presence of synthesized HPMA (Figure 4(b)) or the optimum antiscalant mixture (Figure 4(c)).

The precipitates collected from the experiments without HPMA added showed the characteristic of regular shaped rhombohedra, and the particles’ size was uniform (Figure 4(a)). In contrast, the morphologies of the precipitates changed to framboid spherical shape without sharp edges and acute corners in the presence synthesized HPMA. HPMA molecular could react crystal nucleus of

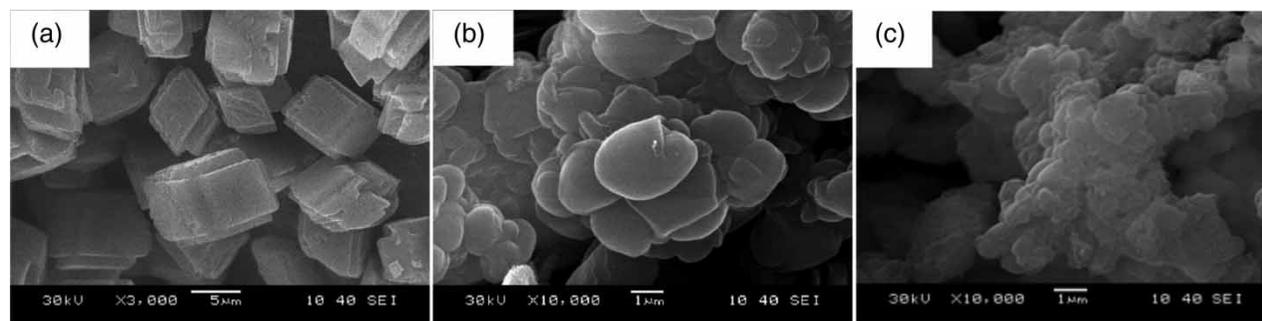


Figure 4 | SEM images of calcium carbonate precipitates: control sample (a), HPMA (b), and the optimum antiscalant mixture (c).

CaCO_3 , and then affect the growth of CaCO_3 crystals (Neira-Carrillo *et al.* 2008). The carboxylate groups on the main chain could react with the active sites on the crystal surface and thus the HPMA molecule could inhibit the CaCO_3 crystal growth by binding the crystal nucleus. Otherwise, through the interaction between carboxylate groups and the active sites of the crystal surface, HPMA molecular chain could change the stereochemical orientation of CaCO_3 growth (Reddy & Hoch 2001). The resulting morphology of crystals is an expression of different growth rates in the various crystallographic directions. Accordingly, precipitates showed framboid spherical shape with a lot of interspaces and the sharp edges and acute corners disappeared totally. HPMA could decrease the adhesion of the precipitates onto the surface of the conical flasks.

The effect of the optimum three-component antiscalant mixture on the calcium carbonate crystal was similar to that of synthesized HPMA. It was, perhaps, because the synthesized HPMA was the main part of the mixture (80%). However, the precipitate in the presence of the mixture showed a loose cotton-shaped appearance with a lot of interspaces and the sharp edges and acute corners disappeared absolutely. The synthesized HPMA and the optimum mixture could decrease the adhesion of the precipitates onto the surface of the conical flasks.

To monitor the structural changes of the CaCO_3 precipitates, X-ray powder diffraction patterns were measured. As shown in Figure 5(a), the diffraction peaks of the precipitates without antiscalant added could be well indexed to the

calcite phase of CaCO_3 including the crystal faces of 012, 104, 110, 113, 202, 018, and 116. This result showed an agreement to that of the SEM images (Figure 4(a)). Both vaterite and calcite phases could be seen when synthesized HPMA or the optimum mixture were used. The vaterite phase was visible including the crystal faces of 100, 101, 102, and 110 besides the calcite phase of CaCO_3 . The intensity of calcite phase peaks was lower than that of blank samples. It was indicated that the synthesized HPMA could inhibit or disturb the calcite growth and induce vaterite growth. Vaterite, as the metastable state of CaCO_3 crystals, was harder to adhere to metal surface and easy to disperse in water solution (Chen *et al.* 2009). The mixture with 10% HEDP and 10% PAA contained showed a much stronger effect on the crystal structure of calcium carbonate precipitates than the synthesized HPMA. In other words, HEDP or PAA enhanced the reaction of synthesized HPMA on calcium carbonate crystal structure.

The mixture of HEDP/HPMA/PAA at the mass ratio of 10/80/10 showed greater influence on the morphologies and crystalline phase of CaCO_3 precipitates. It was demonstrated that a spot of HEDP and PAA enhanced the effect of synthesized HPMA on the crystal of calcium carbonate. The functional groups of HEDP and the COOH groups may react onto the different active points of the crystal nucleus, and thus influence the crystal growth in different ways.

Calcium carbonate scale deposit weighing test

In contrast with calcium carbonate precipitation test, heat exchanger simulated tests were more reasonable to evaluate the scale inhibitors for cooling water systems. The calcium carbonate scale deposit weighing test was designed to investigate the effect of the synthesized HPMA and the optimum three-component antiscalant mixture on the calcium carbonate scale deposit formation on stainless steel surface, which used water bath and electric mixer to simulate industrial conditions.

The antiscalant concentration in the calcium carbonate scale deposit weighing test was designed the same as the calcium carbonate precipitation test. However, the results were different from the calcium carbonate precipitation test results. As shown in Figure 6, the antiscalant efficiency of synthesized HPMA and the optimum three-component antiscalant mixture in the calcium carbonate scale deposit weighing test were less than 40% when the antiscalant concentration was below 10 mg/L. Otherwise, the antiscalant efficiency increased from 25% to 95% when increasing the HPMA concentration from 10 mg/L to 30 mg/L. Similar

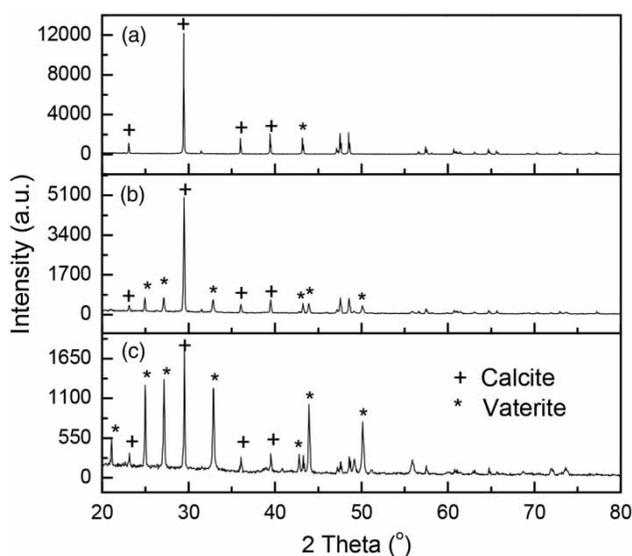


Figure 5 | XRD patterns of calcium carbonate precipitates: control sample (a), synthesized HPMA (b), and the optimum antiscalant mixture (c).

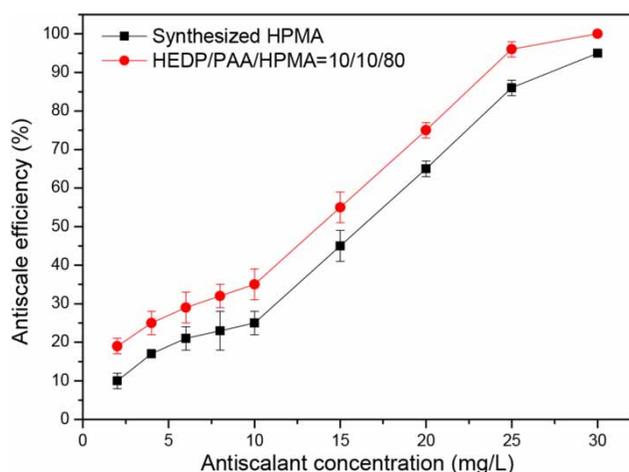


Figure 6 | The antiscale efficiency of calcium carbonate scale deposit weighing test.

trend was obtained for the optimum antiscalant mixture. The optimum antiscalant mixture showed higher antiscale efficiency than synthesized HPMA at the same concentration. It was indicated that the optimization results were suitable for the calcium carbonate scale deposit weighing test. In other words, the calcium carbonate scale deposit weighing test confirmed that the optimum antiscalant mixture were suitable for mineral scale control in a cooling water system. Also, high concentration of synthesized HPMA or the optimum mixture to 30 mg/L could provide excellent antiscale efficiency. This result could provide some suggestion about high concentration use of HPMA in industrial cooling water systems.

To further investigate the inhibition effect of the synthesized and optimized antiscalant mixture on calcium

carbonate scale deposit, SEM images of stainless steel specimen surface were obtained and are shown in Figure 7. When the concentration of synthesized HPMA was at 10 mg/L, large calcium carbonate scale deposit was detected on the stainless steel specimen surface. However, in contrast with the control sample, the morphology of the deposit on the steel surface changed to an irregular shape without sharp edges and acute corners in the presence of synthesized HPMA. Also, the optimum three-component mixture showed stronger effect on the morphology of the calcium carbonate deposit on the stainless steel surface. The deposit in the presence of the mixture showed a loose cotton-shaped appearance with a lot of interspaces. This result was in agreement with the morphology analysis of calcium carbonate precipitates in the calcium carbonate precipitation test. When the concentration of synthesized HPMA and the optimum antiscalant mixture increased to 20 mg/L or 30 mg/L, deposit decreased significantly. Especially at 30 mg/L, only some microparticles were visible on the stainless steel surface. The SEM image analysis indicated that high concentration (30 mg/L) of synthesized HPMA and the optimum antiscalant mixture was necessary to control calcium carbonate mineral scale in cooling water system.

CONCLUSIONS

The mixture of HEDP, and PAA and synthesized HPMA was optimized by using simplex lattice mixture design of Design-Expert software through calcium carbonate

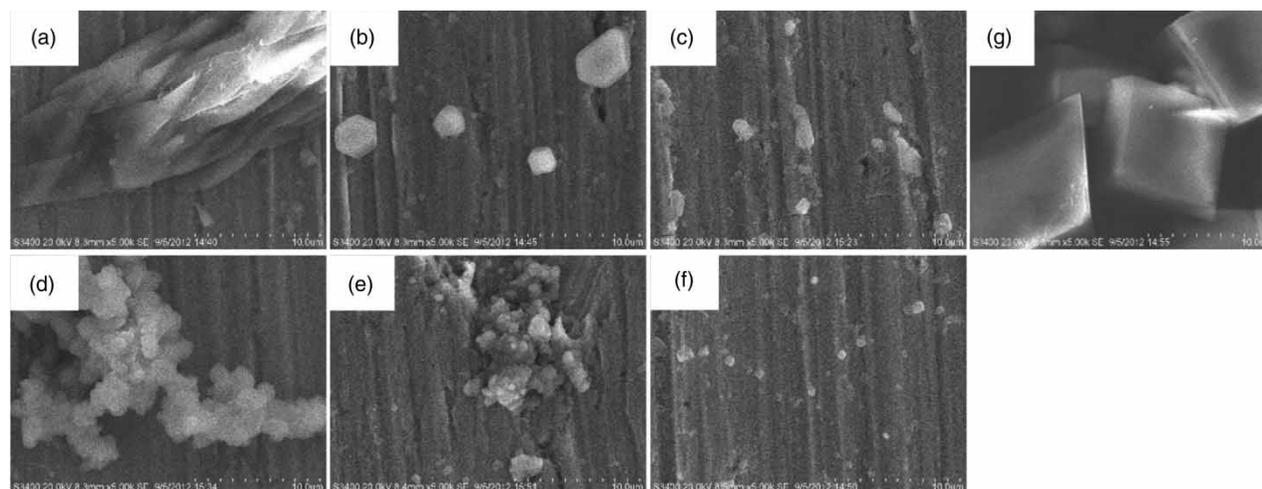


Figure 7 | SEM images of calcium carbonate scale deposit on steel surface: (a), (b) and (c) are for HPMA 10 mg/L, 20 mg/L and 30 mg/L; (d), (e) and (f) are for optimum antiscalant mixture 10 mg/L, 20 mg/L and 30 mg/L; (g) is for control sample.

precipitation method. The optimum mass ratio of HEDP, PAA and synthesized HPMA was obtained at 10/10/80.

Under the calcium carbonate precipitation test, the optimum showed much better antiscaling efficiency (78% for synthesized HPMA and 84% for the optimum mixture). The synthesized HPMA could disturb the crystal growth of calcium carbonate and then affect the morphology and crystal structure of the calcium carbonate crystal precipitates. The optimum showed a much stronger effect on the morphology and crystal structure of the calcium carbonate crystal precipitates.

Under the calcium carbonate scale deposit test, the optimum antiscalant mixture showed excellent performance on controlling the calcium carbonate deposition onto the stainless steel surface. The antiscaling efficiency increased significantly from less than 40% to more than 95% when increasing the antiscalant concentration from 10 mg/L to 30 mg/L.

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