*Desalination and Water Treatment*
www.deswater.com
doi: 10.5004/dwt.2022.28457

259 (2022) 37–44
May

# Research on the preparation of a scale inhibitor PESA-ESA-AMPS based on polyepoxysuccinic acid

Lian-gang Hou[a,*], Yi-tao Liu[b], Jun Li[c,*]

[a]*Infrastructure Department, China Construction First Group Construction & Development Co., Ltd., Beijing 100102, China, email: houliangang@163.com (L.-g. Hou)*
[b]*Design Institute II, China Shipbuilding Industry Corporation International Engineering Co., Ltd., Beijing 100121, China, email: 1341145722@qq.com (Y.-t. Liu)*
[c]*Faculty of Architecture, Civil and Transportation Engineering, Beijing University of Technology, Beijing 100124, China, email: bjutlijun@sina.com (J. Li)*

Received 14 September 2021; Accepted 27 March 2022

**ABSTRACT**

In order to improve the scale inhibition efficiency of polyepoxysuccinic acid (PESA), this study optimizing, modifying the synthetic steps of scale inhibitor PESA, and obtained a novel scale inhibitor PESA-ESA-AMPS by using a mixture compounds of modified PESA and ESA-AMPS. When the dosage of PESA-ESA-AMPS was 1% (m/M), the scale inhibition rate of PESA-ESA-AMPS to $Ca^{2+}$ and $Mg^{2+}$ in the actual circulating cooling water exceeded 80% and 70%, respectively. It was calculated that 10 g PESA-ESA-AMPS could achieve better scale inhibition effect in 1t circulating cooling water. Scanning electron microscopy observation shown that when PESA-ESA-AMPS was added into the circulating cooling water, the scale was dispersed into a soft and amorphous form, without obvious hexagonal shape, mainly in granular and small spheres, well dispersed and the volume was also greatly reduced. PESA-ESA-AMPS was an environmental-friendly and low-cost scale inhibitor for circulating cooling water system, it is hoped that this research could promote the application of scale inhibitor PESA-ESA-AMPS in the field of water treatment such as circulating cooling water systems.

*Keywords:* Polyepoxysuccinic acid (PESA); Scale inhibition; Corrosion inhibition; Circulating cooling water

## 1. Introduction

Scaling is one of the main problems in water treatment fields such as circulating cooling water systems [1–5], boiler heating supply systems, seawater desalination systems, and petroleum well pipeline systems [6–8]. Especially with the continuous improvement of industrial circulating cooling water concentration ratio, scaling and corrosion problems have seriously affected the industry development [9–12]. Adding corrosion and scale inhibitors to industrial circulating cooling water is an important and economical effective method to solve scaling and corrosion [13–16]. Thus, the research on new type corrosion and scale inhibitors has become an important focus in water treatment field [17,18].

Polyepoxysuccinic acid (PESA) is a kind of novel scale inhibitor characterized by high scale inhibiting efficiency [19], non-phosphorus, non-nitrogenous [20], good thermal stability and biodegradability [21], and could better adapt to high alkali, high hardness water system, it is a representative of environmental friendly efficient scale inhibitor [22,23] and it has received extensive attention from the water treatment industry [24–26]. Some scientific reports have proved that PESA has good inhibitory performance on

* Corresponding authors.

$CaCO_3$ scale and poor dispersing performance on $Ca_3(PO_4)_2$ scale, $CaSiO_3$ scale and $Zn^{2+}$ [27–29]. Because the molecular structure of PESA is mainly –COOH and the functional group is single, which limits the further applications of PESA. Mixing PESA with other polymers could optimize the scale inhibition performance of PESA theoretically, however, it has attracted relatively little attention.

Here, we optimizing, modifying the synthetic steps of scale inhibitor PESA, and a scale inhibitor PESA-ESA-AMPS was obtained by using a mixtured compounds of modified PESA and ESA (epoxysuccinic acid, ESA)-AMPS (2-acrylamide-2-methylpropanesulfonic acid, AMPS). In this study, the scale inhibition performance of PESA-ESA-AMPS was explored and verified with actual circulating cooling water, and characterized the scale by scanning electron microscope (SEM). Through this research, we hope it could promote the application of scale inhibitor PESA-ESA-AMPS in the field of water treatment fields.

## 2. Materials and methods

### 2.1. Synthesis of the PESA

Fig. 1 is the reaction process, and the preparation steps of PESA are as follows [19,29]: 9.8 g maleic anhydride and 30 mL deionized water was added into a three-necked flask equipped with a thermometer, a condenser, a conical dropping funnel and a constant-speed stirring device. 7~8 mL 50% sodium hydroxide solution was added dropwise under stirring. Heated and added 0.34 g sodium tungstate catalyst when the temperature rised to 55°C, then dropped 10~12 mL hydrogen peroxide in 30 min, reacted for about 1 h at 75°C~95°C to generate epoxysuccinic acid (ESA). Then solid sodium hydroxide was used as a polymerization agent to polymerize for 1.5~3.5 h under alkaline conditions, and light-yellow viscous liquid was obtained which is PESA after the reaction over. All chemical reagents are A.R. grade.

### 2.2. Modified of the PESA

In this study, sulfonic acid groups were introduced to carboxylic acid polymers, epoxysuccinic acid (ESA) and 2-acrylamide-2-methylpropanesulfonic acid (AMPS) were copolymerized to modify PESA. The modification method is shown in Fig. 2. The recrystallized ESA, AMPS and distilled water was added into a three-necked flask equipped with a condenser and thermometer. The solution was heated to a certain temperature and adjust the pH to alkaline with 50% NaOH solution, then the initiator ammonium persulfate was added and reacted for a period of time, and the white crystals precipitated are ESA-AMPS.

### 2.3. Analysis of actual circulating cooling water quality

The elemental analysis results of the actual circulating cooling water quality used in this research is shown in Table 1.

### 2.4. SEM observation

In this study, scanning electron microscopy (SEM, Quanta 250FEG, FEI) was used to observe [30] and analyze the morphology of scale samples. Add the scale inhibitor or not into the scaling actual circulating cooling water samples respectively, dry the scale particles at 105°C and observe the scale samples by SEM after gold spraying.

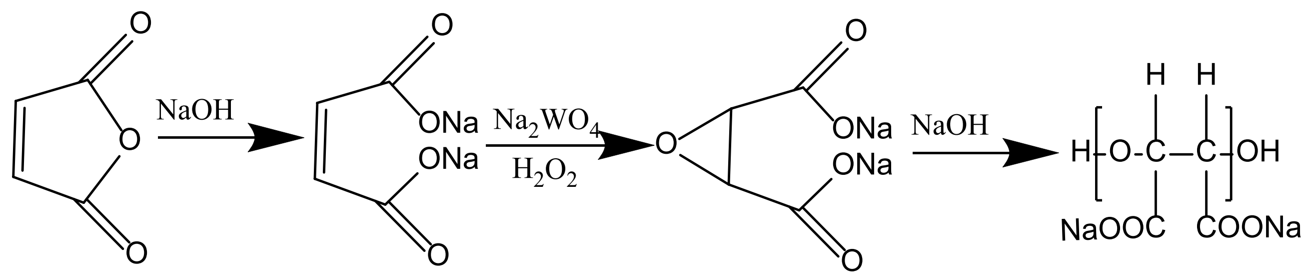


Fig. 1. Reaction process during the preparation of PESA.

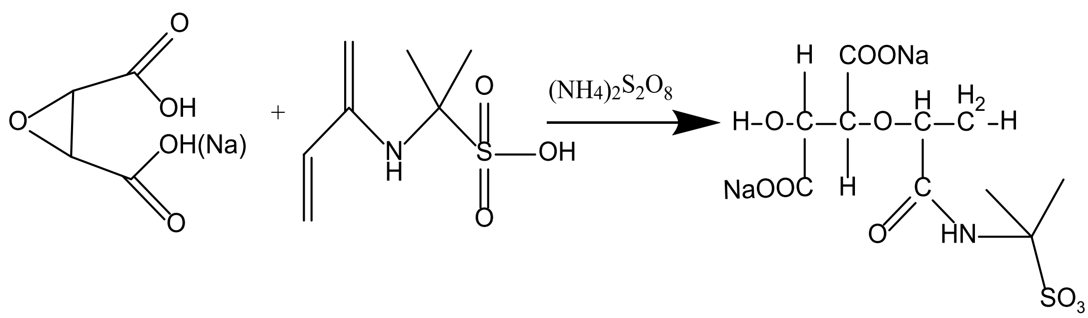


Fig. 2. Reaction process during the modified of PESA.

## 3. Results and discussion

### *3.1. Research on the influencing factors of PESA yield and scale inhibition performance*

PESA was prepared in the experiment, an orange-yellow viscous liquid. To further optimize the preparation steps of PESA, the polymerization temperature, polymerization time and $H_2O_2$ dosage were selected as the investigating factors, and carried out a single factor experiment. The best conditions for the synthesis of PESA were explored by measuring the yield of PESA and the scale inhibition rate of PESA to $CaCO_3$.

The study investigated the effect of temperature, polymerization time and $H_2O_2$ dosage on the yield of PESA and the scale inhibition performance of $CaCO_3$. As Fig. 3a shows, the yield of PESA decreases with temperature increasing, and the yield decreases sharply when the temperature is higher than 85°C. This is because the decomposition of $H_2O_2$ and the generation of side reactions will be accelerated when the temperature is higher, resulting in a decrease of yield. It can be seen from Fig. 3 that PESA has the best scale inhibition effect on $CaCO_3$ at 85°C, lower or higher temperature will affect the scale inhibition performance, because the scale inhibition effect is related to the PESA degree of polymerization. ESA is a free radical polymerization and the free radical activity is poor when the temperature is too low, and the polymerization degree of polymer is low due to the low collision

Table 1
Water quality analysis of the circulating cooling water

| Test index | Contents (mg/L) | Test index | Contents (mg/L) |
|---|---|---|---|
| Na | 291.6300 | B | 0.4901 |
| S | 93.4190 | Sr | 0.3735 |
| K | 65.7510 | Fe | 0.0245 |
| Ca | 85.4700 | Li | 0.0882 |
| Mg | 15.7550 | Al | 0.0727 |
| Si | 5.2104 | Mo | 0.0673 |
| P | 0.6362 | Ba | 0.0397 |
| Nd | 0.6121 | Zn | 0.0534 |

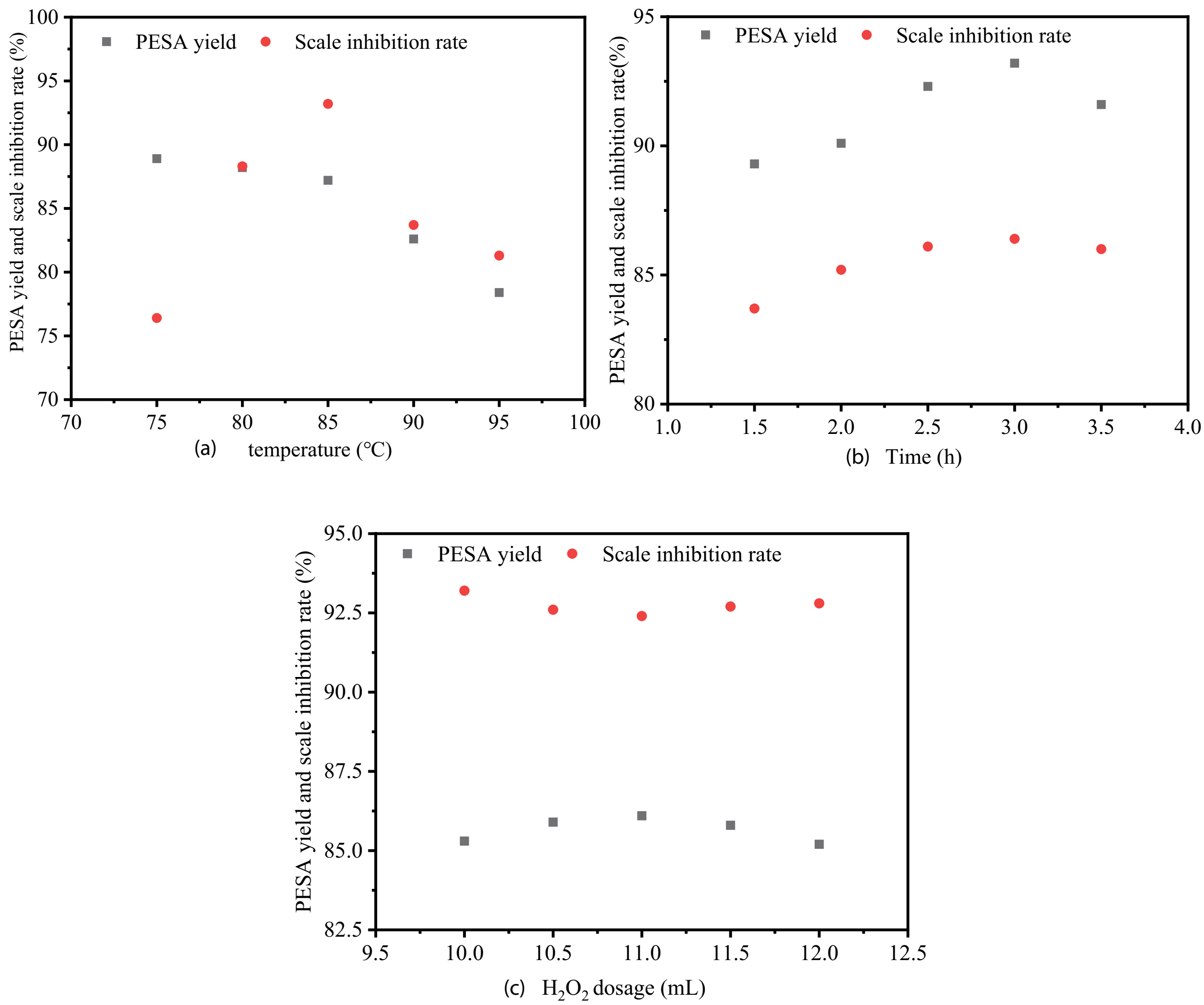


Fig. 3. The influence on the yield and scale inhibition rate of PESA, (a) temperature, (b) time and (c) $H_2O_2$ dosage.

probability. Simultaneously, the polymerization degree of the polymer is too high at higher temperature, which will affect the scale inhibition performance. Fig. 3b shows the effect of time on PESA yield and $CaCO_3$ inhibition rate. The yield of PESA and $CaCO_3$ inhibition rate increases with time increase within 3 h, and it reaches the maximum when time is 3 h. The scale inhibition rate of PESA reaches 92.3% at 3 h, and the yield and $CaCO_3$ inhibition rate decreased after 3 h. The reaction is incomplete when the reaction time is less than 3 h, and the PESA yield and inhibition rate on $CaCO_3$ is low. The polymerization of PESA is too high when the reaction time exceeds 3 h, which will affect the scale inhibition performance. It can be seen from Fig. 3c that the PESA yield increases at first and then decreases with increasing of $H_2O_2$ dosage, while the scale inhibition performance of PESA decreases at first and then increases. The scale inhibition rate of PESA is the lowest and the yield reaches the maximum when the $H_2O_2$ dosage is 11 mL. The best preparation conditions of PESA and the best scale inhibition conditions of PESA for $CaCO_3$ are obtained through the single factor experiments, the scale inhibition rate of PESA for $CaCO_3$ exceeds 92% under the following conditions: the reaction time is 3~3.5 h with 85°C and the dosage of $H_2O_2$ is 10 mL.

### *3.2. Modification of the PESA*

The functional group of PESA is mainly single carboxyl functional group, its effect in inhibiting calcium phosphate scale is not significant, and PESA is easy to produce insoluble polymer calcium gel when calcium concentration is higher, so PESA needs to be modified. Introducing sulfonate groups into carboxylic acid polymers could effectively improve the ability of inhibiting calcium phosphate [25].

Epoxysuccinic acid (ESA) and 2-acrylamide-2-methylpropanesulfonic acid (AMPS) were copolymerized to modify PESA in this study. PESA and ESA-AMPS were applied to inhibiting $CaCO_3$, $Ca_3(PO_4)_2$, and stabilizing zinc salt, and compared their scale inhibition and stability performance. It can be seen from Fig. 4 that the $Ca_3(PO_4)_2$ scale inhibition performance and $Zn^{2+}$ stability performance has been significantly improved after the introduction of sulfonic acid groups in PESA. The scale inhibition rate of ESA-AMPS to $Ca_3(PO_4)_2$ reached 77%, which is higher than PESA by 2~5 times, the stability rate of ESA-AMPS to $Zn^{2+}$ reached 75%, which is 1.5~3 times than PESA. However, the scale inhibition performance of ESA-AMPS on $CaCO_3$ is lower than PESA. Therefore, the modified PESA needs further modification to optimize its performance.

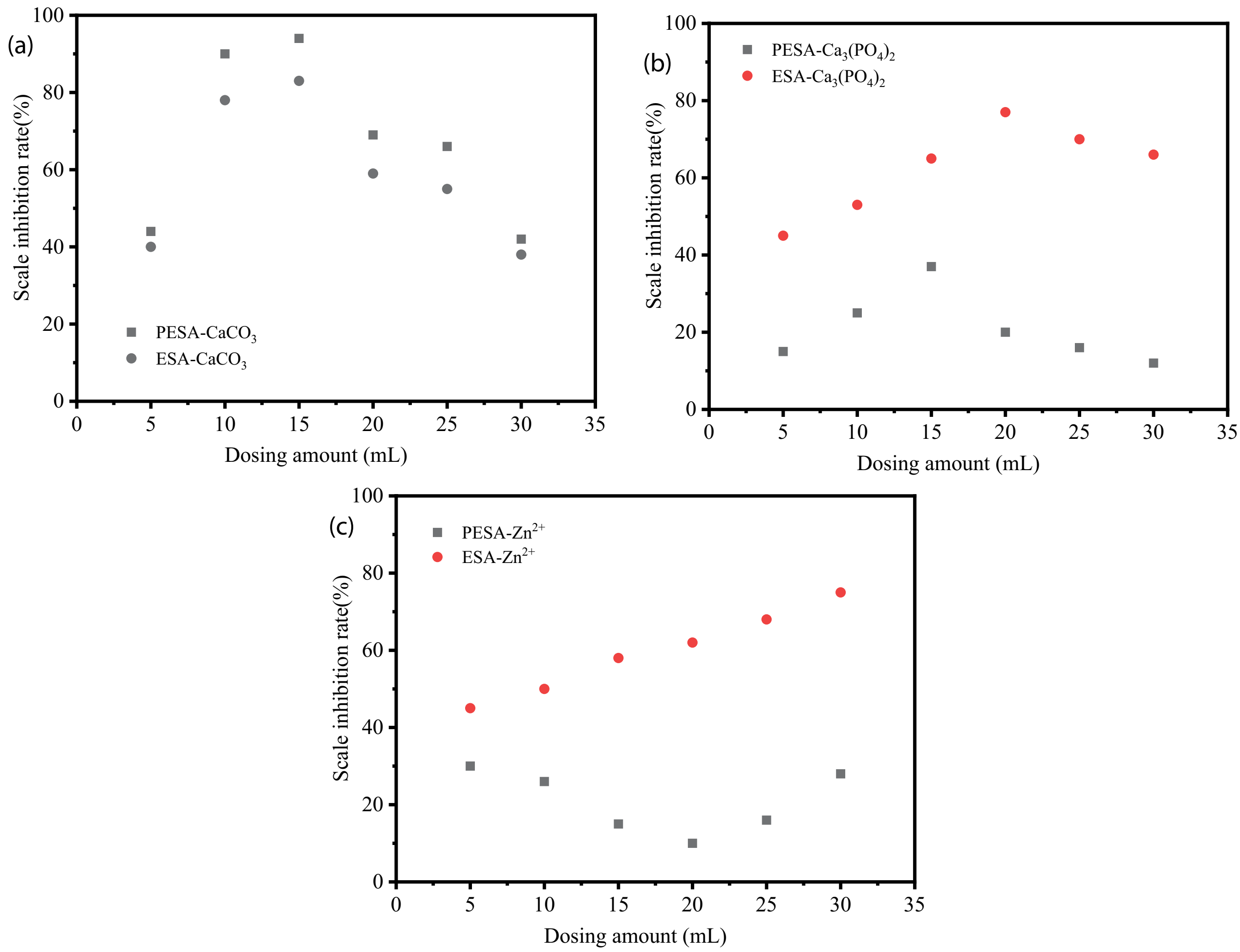


Fig. 4. The scale inhibition performance of modified PESA on (a) $CaCO_3$, (b) $Ca_3(PO_4)_2$ and (c) $Zn^{2+}$.

PESA has a better anti-scaling effect on $CaCO_3$, and ESA-AMPS has better anti-scaling performance against $Ca_3(PO_4)_2$ and stable $Zn^{2+}$ performance, so PESA and ESA-AMPS were mixtured, and a novel type of scale inhibitor with better scale inhibition performance was obtained in this study. The research explored the best ratio of PESA and ESA-AMPS. Table 2 shows the scale inhibition effect of the PESA copolymer under various ratios, and the ratio shown in the table is the mass ratio of PESA:ESA-AMPS. It can be seen from Fig. 5 that the mixtured compound has a good scale inhibition performance on $CaCO_3$ and $Ca_3(PO_4)_2$ when the ratio of PESA:ESA-AMPS was 1:2. Therefore, the mixtured compounds of PESA and ESA-AMPS with the mass ratio 1:2 was used to form a novel scale inhibitor which labeled PESA-ESA-AMPS.

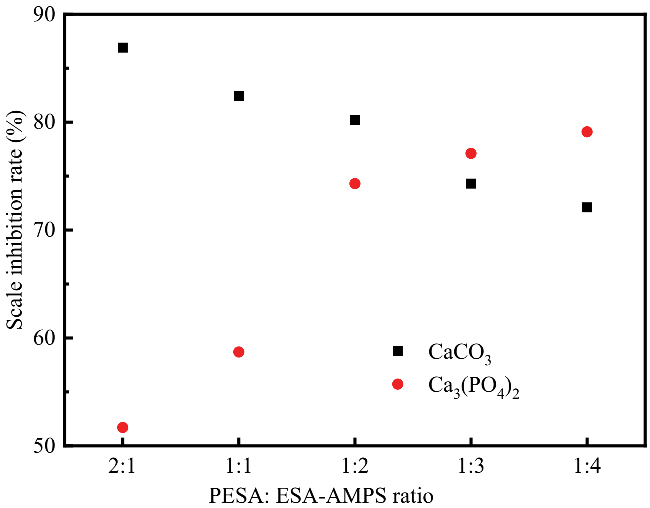


Fig. 5. The scale inhibition performance of PESA and ESA-AMPS at different ratios.

Table 2
Scale inhibition effect of PESA physical compounding under different ratio

| PESA:ESA-AMPS ratio | $CaCO_3$ inhibition rate (%) | $Ca_3(PO_4)_2$ inhibition rate (%) |
|---|---|---|
| 2:1 | 86.9 | 51.7 |
| 1:1 | 82.4 | 58.7 |
| 1:2 | 80.2 | 74.3 |
| 1:3 | 76.3 | 77.1 |
| 1:4 | 72.1 | 79.1 |

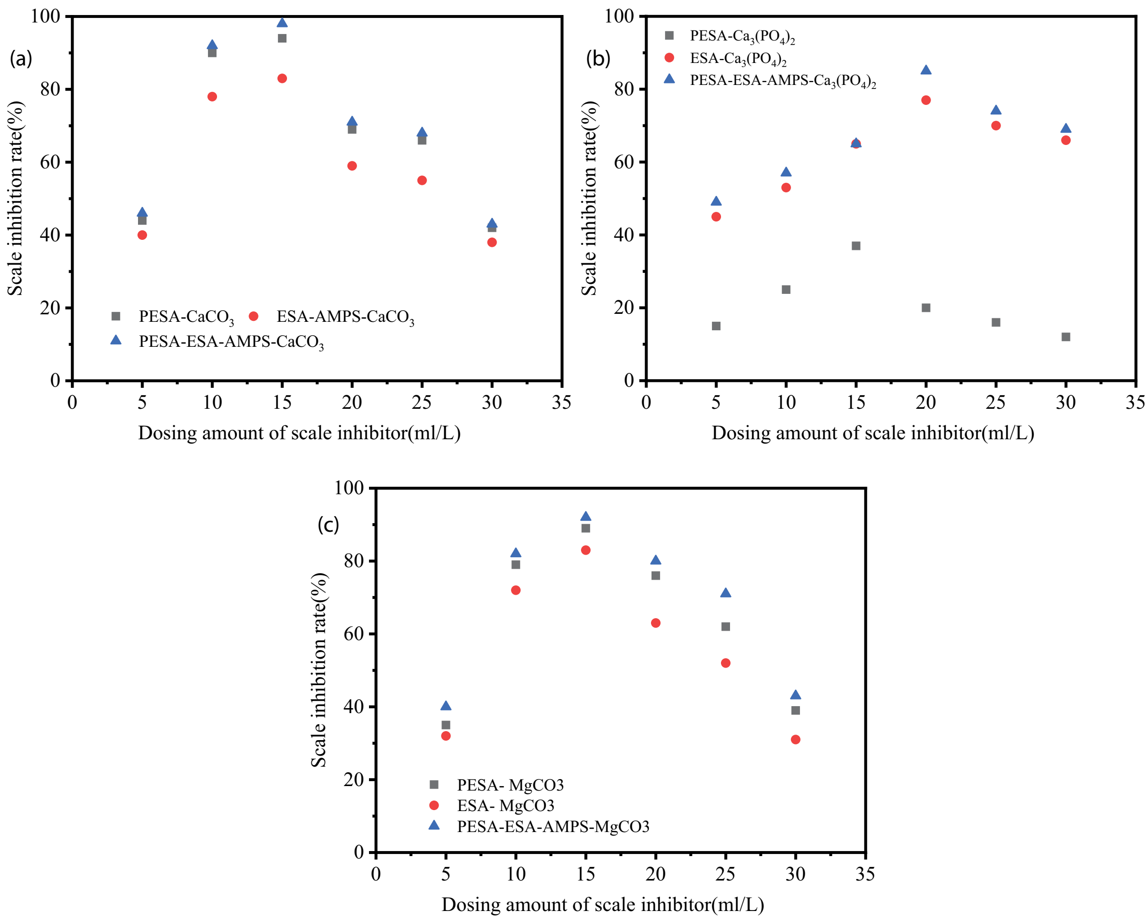


Fig. 6. The scale inhibition performance of copolymer inhibitor on (a) $CaCO_3$, (b) $Ca_3(PO_4)_2$ and (c) $MgCO_3$.

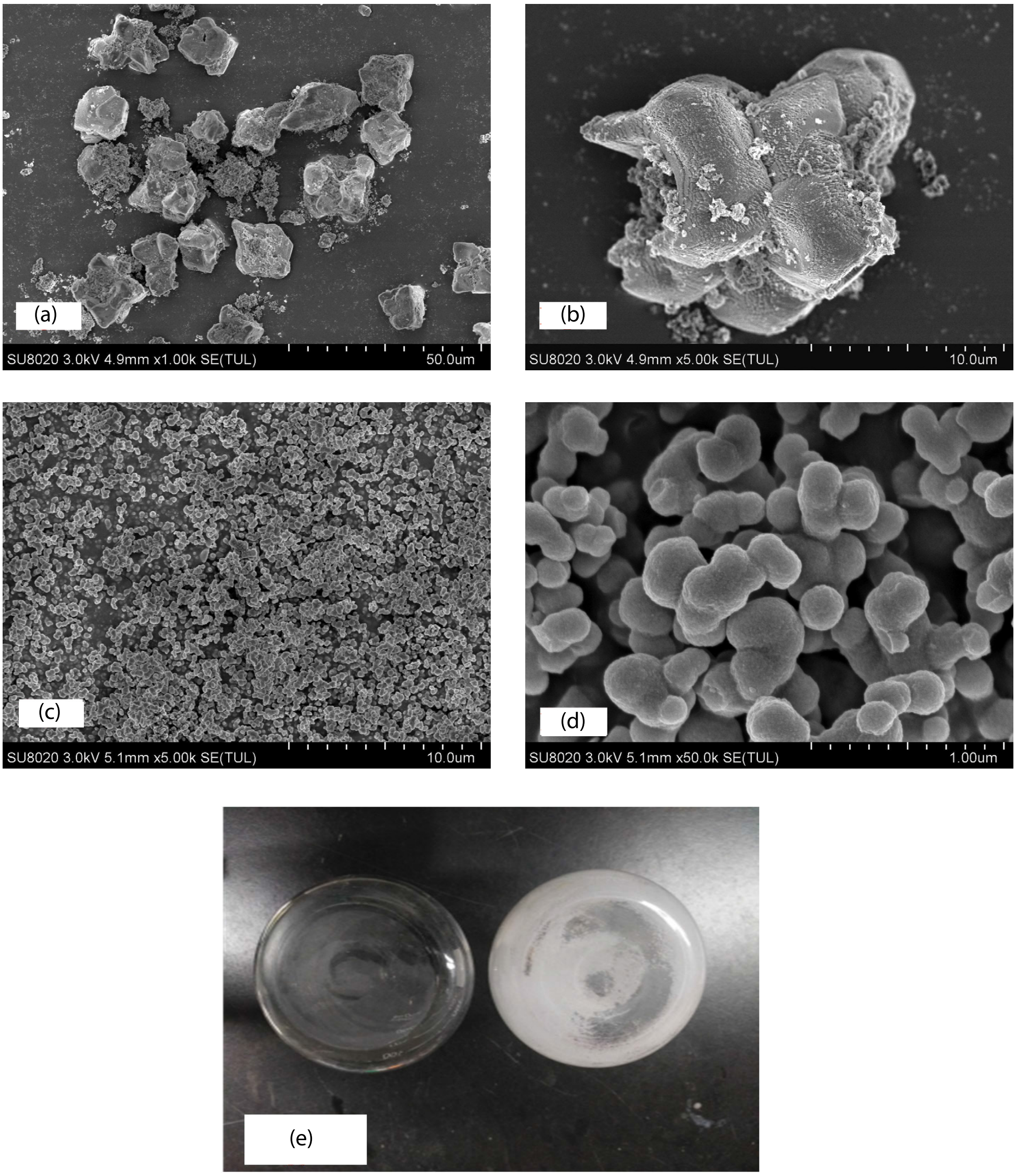


Fig. 7. SEM image and performance comparison photos of PESA-ESA-AMPS in actual cooling water scale when added or not.

According to the analysis results of water quality elements, the circulating cooling water samples used in the research mainly contains calcium and magnesium, so PESA-ESA-AMPS was used to conduct further research on calcium scale and magnesium scale. It can be seen from Fig. 6 that the PESA-ESA-AMPS has better scale inhibition performance on $CaCO_3$ and $MgCO_3$ than ESA-AMPS, and the scale inhibition effect to $Ca_3(PO_4)_2$ was better than unmodified PESA. That is to say, PESA-ESA-AMPS has better scale inhibition effects on carbonates and phosphates, and the scale inhibitors performance of PESA has been improved.

### *3.3. Application research of the modified PESA*

Actual circulating cooling water was used to verify the application performance of the novel scale inhibitor PESA-ESA-AMPS. It can be seen from Table 1 that the main elements which could produce scale in the circulating cooling water was calcium and magnesium ions. Therefore, PESA-ESA-AMPS was mainly to prevents the formation of calcium and magnesium in actual circulating cooling water.

The PESA-ESA-AMPS was applied to actual circulating cooling water sample, Fig. 7a and b are the morphology

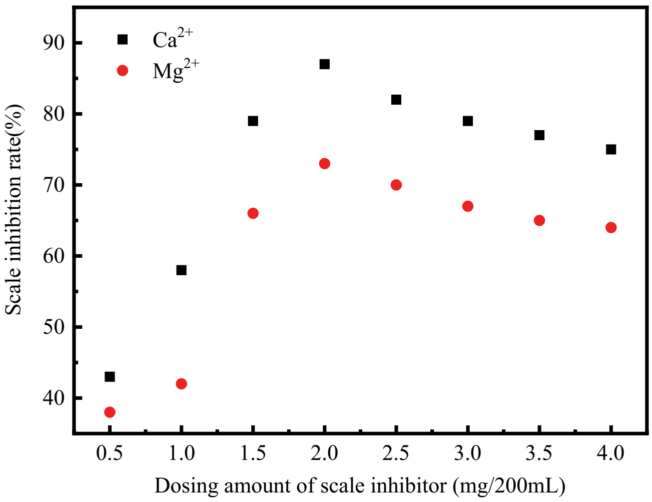


Fig. 8. The scale inhibition performance of PESA-ESA-AMPS in actual circulating cooling water.

photos of scale formed with no scale inhibitor added while (c and d) with scale inhibitor added. Fig. 7e is the comparison performance photo of PESA-ESA-AMPS in actual cooling water scale with added or not. According to the SEM photos, the scale particles present a regular hexagonal crystal system with no PESA-ESA-AMPS added, indicating the crystal form of scale in this environment is mainly calcite, the crystal size is large, and most of them were clustered together which was easier to form dense hard scale. When a certain amount of PESA-ESA-AMPS was added to the circulating cooling water, the scale was dispersed into soft and amorphous shape, without obvious hexagonal shape, mainly in granular and small spheres, well dispersed and the volume was also greatly reduced.

The scale inhibition performance on calcium ions and magnesium ions is shown in Fig. 8. When adding different amounts of PESA-ESA-AMPS to 200 mL actual water sample. As can be seen from Fig. 8, adding 1.5~2.5 mg scale inhibitor into 200 mL actual circulating cooling water has better scale inhibition performance. When the dosage was 1% (m/M, 200 mL water sample with 2 mL scale inhibitor), the scale inhibition rate of PESA-ESA-AMPS to $Ca^{2+}$ and $Mg^{2+}$ in the circulating cooling water exceeded 80% and 70%, respectively. In other words, 10 g PESA-ESA-AMPS could achieve better scale inhibition effect in 1t circulating cooling water. Therefore, PESA-ESA-AMPS was an environmental-friendly and low-cost scale inhibitor for circulating cooling water system.

## 4. Conclusions

It optimizing, modifying the synthetic steps of scale inhibitor PESA, and obtained a novel scale inhibitor PESA-ESA-AMPS by using a mixtured compounds of modified PESA and ESA-AMPS in this study. When the dosage was 1% (m/M), the scale inhibition rate of PESA-ESA-AMPS to calcium and magnesium ions in the actual circulating cooling water exceeds 80% and 70%, respectively. 10 g PESA-ESA-AMPS could achieve better scale inhibition effect in 1t circulating cooling water. PESA-ESA-AMPS was an environmental-friendly and low-cost scale inhibitor for circulating cooling water system, and it is hoped that this research could promote the application of scale inhibitor PESA-ESA-AMPS in the field of water treatment.

## Acknowledgements

This work was supported by the Major Science and Technology Program for Water Pollution Control and Treatment (No. 2015ZX07202-013).

## Declaration of competing interest

There are no conflicts of interest to declare.

## References

[1] B. Yang, C. Chen, J. Zhou, Z. Zhao, Economic analysis of circulating water system based on grey system theory, IOP Conf. Ser.: Earth Environ. Sci., 227 (2019) 1–8, doi: 10.1088/1755-1315/227/4/042037.
[2] L.L. Wei, K.N. Qin, Q.L. Zhao, D.R. Noguera, M. Xin, C.C. Liu, N. Keene, K. Wang, F.Y. Cui, Utilization of artificial recharged effluent as makeup water for industrial cooling system: corrosion and scaling, Water Sci. Technol., 73 (2016) 2559–2569.
[3] C. He, Z. Tian, B. Zhang, Y. Lin, X. Chen, M. Wang, F. Li, Inhibition effect of environment-friendly inhibitors on the corrosion of carbon steel in recirculating cooling water, Ind. Eng. Chem. Res., 54 (2015) 1971–1981.
[4] F. Liu, X. Lu, W. Yang, J. Lu, H. Zhong, X. Chang, C. Zhao, Optimizations of inhibitors compounding and applied conditions in simulated circulating cooling water system, Desalination, 313 (2013) 18–27.
[5] C.M. Chen, Y. Wang, S.T. Liu, R.R. Feng, X.J. Gu, C.X. Qiao, Research on the application of compound microorganism preparation in reusing urban reclaimed water in circulating cooling water system, Water Sci. Technol., 80 (2019) 1763–1773.
[6] Y. Zhao, L, Jia, K. Liu, P. Gao, H. Ge, L. Fu, Inhibition of calcium sulfate scale by poly (citric acid), Desalination, 392 (2016) 1–7.
[7] Y. Song, X. Gao, C. Gao, Evaluation of scaling potential in a pilot-scale NF-SWRO integrated seawater desalination system, J. Membr. Sci., 443 (2013) 201–209.
[8] Y.Y. Chen, Y.M. Zhou, Q.Z. Yao, Q.L. Nan, M.J. Zhang, W. Sun, Performance on calcium scales inhibition in the presence of a novel double-hydrophilic block terpolymer, Desal. Water Treat., 161 (2019) 66–75.
[9] Z. Mohammadi, M. Rahsepar, Characterization of Mazuj galls of *Quercus infectoria* tree as green corrosion and scale inhibitor for effective treatment of cooling water systems, Res. Chem. Intermed., 44 (2018) 2139–2155.
[10] X. Guo, F. Qiu, K. Dong, X. Zhou, J. Qi, Y. Zhou, D. Yang, Preparation, characterization and scale performance of scale inhibitor copolymer modification with chitosan, J. Ind. Eng. Chem., 18 (2012) 2177–2183.
[11] Y.A. Roomi, K.F. Hussein, M.R. Riazi, Inhibition efficiencies of synthesized anhydride based polymers as scale control additives in petroleum production, J. Pet. Sci. Eng., 81 (2012) 151–160.
[12] H.C. Wang, J.J. Yang, C.R. Li, M.J. Zhu, Q.Y. Wu, M.Y. Wu, J.N. Zhang, Study on the performance of $CaSO_4$ scale for phosphorus-free modified PEG scale inhibitor in cooling water system, Desal. Water Treat., 151 (2019) 20–25.
[13] Z. Liu, N. Li, M. Yan, R. Guo, Z. Liu, The research progress of water treatment technology on recirculated cooling water, IOP Conf. Ser.: Earth Environ. Sci., 508 (2020) 1–5.
[14] B. Zhang, C. He, C. Wang, P. Sun, F. Li, Y. Lin, Synergistic corrosion inhibition of environment-friendly inhibitors on the corrosion of carbon steel in soft water, Corros. Sci., 94 (2015) 6–20.

[15] D. Liu, W. Dong, F. Li, F. Hui, J. Ledion, Comparative performance of polyepoxysuccinic acid and polyaspartic acid on scaling inhibition by static and rapid controlled precipitation methods, Desalination, 304 (2012) 1–10.
[16] X. Ouyang, X. Qiu, H. Lou, D. Yang, Corrosion and scale inhibition properties of sodium lignosulfonate and its potential application in recirculating cooling water system, Ind. Eng. Chem. Res., 45 (2006) 5716–5721.
[17] J.D. Zhao, Z.A. Liu, E.J. Zhao, Combined effect of constant high voltage electrostatic field and variable frequency pulsed electromagnetic field on the morphology of calcium carbonate scale in circulating cooling water systems, Water Sci. Technol., 70 (2014) 1074–1082.
[18] Z. Liu, X. Wang, Z.F. Liu, Synthesis and properties of the ESA/AMPS copolymer, Sci. Technol. Eng., 164 (2013) 194–198.
[19] H. Huang, Q. Yao, Q. Jiao, B. Liu, H. Chen, Polyepoxysuccinic acid with hyper-branched structure as an environmentally friendly scale inhibitor and its scale inhibition mechanism, J. Saudi Chem. Soc., 23 (2019) 61–74.
[20] H.H. Li, Z.F. Liu, L.H. Zhang, M.F. Yan, X.H. Li, Synergistic scale inhibition performance of polyepoxysuccinic acid with high-voltage electrostatic field, Asian J. Chem., 25 (2013) 8393–8396.
[21] W.Y. Shi, C. Ding, J.L. Yan, X.Y. Han, Z.M. Lv, W. Lei, M.Z. Xia, F.Y. Wang, Molecular dynamics simulation for interaction of PESA and acrylic copolymers with calcite crystal surfaces, Desalination, 291 (2012) 8–14.
[22] C. Chen, Y. Hu, H. Zhu, W. Sun, W. Qin, R. Liu, Z. Gao, Inhibition performance and adsorption of polycarboxylic acid in calcite flotation, Miner. Eng., 133 (2019) 60–68.
[23] Z. Quan, Y. Chen, X. Wang, C. Shi, Y. Liu, C. Ma, Experimental study on scale inhibition performance of a green scale inhibitor polyaspartic acid, Sci. China Ser. B., 51 (2008) 695–699.
[24] Y. Chen, Y. Zhou, Q. Yao, Q. Nan, M. Zhang, W. Sun, Inhibition, dispersion and corrosion performance of a novel modified polyepoxysuccinic acid, Desal. Water Treat., 173 (2020) 223–230.
[25] T. Gu, P. Su, X. Liu, J. Zou, X. Zhang, Y. Hu, A composite inhibitor used in oilfield: MA-AMPS and imidazoline, J. Pet. Sci. Eng., 102 (2013) 41–46.
[26] Z.Y. Liang, Q.M. Li, C.Z. Gao, Z.F. Cheng, X.J. Qi, Determination of polyepoxysuccinic acid in circulating water by spectrometric method, Desal. Water Treat., 57 (2016) 4952–4959.
[27] J. Chen, F. Chen, J. Han, M. Su, Y. Li, Evaluation of scale and corrosion inhibition of modified polyaspartic acid, Chem. Eng. Technol., 43 (2020) 1048–1058.
[28] Y. Chen, Y. Zhou, Q. Yao, Q. Nan, M. Zhang, W. Sun, Inhibition and biodegradability performance of modified polyepoxysuccinic acid as a scale inhibitor against calcium carbonate, Desal. Water Treat., 147 (2019) 211–221.
[29] Y. Sun, W. Xiang, Y. Wang, Study on polyepoxysuccinic acid reverse osmosis scale inhibitor, J. Environ. Sci. (China), 21 Suppl (2009) 73–75.
[30] L.G. Hou, J. Li, F.Y. Sun, X.Y. Zhang, Y. Liu, High-efficiency denitrification for steel wastewater treatment by immobilized bacteria, Desal. Water Treat., 211 (2021) 117–122.