Synthesis, Scale And Corrosion Inhibition of Polyaspartic Acid Derivative

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Abstract—Polyaspartic acid derivative (PASP-SEA-ASP) was prepared from polysuccinimide (PSI) that was thermal condensation polymer of aspartic acid (ASP), taurine (SEA) and ASP. The structure of polyaspartic acid derivative was characterized by means of FTIR. The property of scale inhibition of PASP-SEA-ASP by static experment and weight loss method for corrosion inhibition efficiency were studied. Calcium carbonate crystals in scale samples and corrosive test pieces were analysed by means of SEM. The results showed that under Ca^{2+} 400 mg/L, HCO_3^- 800 mg/L and polyaspartic acid derivative 4 mg/L, the scale inhibition rate of polyaspartic acid derivative can reach 67.42%. And it also possessed better corrosion inhibition performance and the corrosion inhibition rate can reach 67.53%. Measuring results of SEM showed that polyaspartic acid derivative could distort calcium carbonate crystallite and made calcium carbonate crystallite more dispersive. Measured by SEM, the test piece was immersed in solution with polyaspartic acid derivative has little pits on its surface. This study demonstrated the potential of PASP-SEA-ASP to inhibit both corrosion and scale formation in industrial circulating cooling water systems.

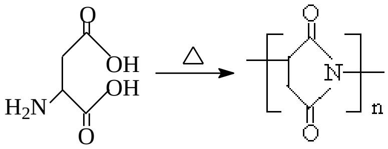
Keywords-water treatment; polyaspartic acid; polyaspartic acid derivative; scale inhibition; corrosion inhibition

I. INTRODUCTION

In industrial cooling water system, mineral ions in water, such as bicarbonate and calcium, may concentrate to form scale in heat transfer equipment. In order to control scale, numerous chemicals have been used widely in the cooling water system. With the increase of environmental awareness, people pay much more attention to the study of new green scale inhibitors all over the world [1-3]. Polyaspartic acid (PASP) is a non-phosphorus based biodegradable polyaminoacid, which has been used as an environment-friendly scale and corrosion inhibitor for fresh-water applications. It was the representative of the no-phosphorus biodegradable environmental friendly water treatment agents [4]. Although PASP had the function of chelating and dispersion, its chelating and dispersing performance was worse than acrylic acid and maleic acid polymers, especially, when applied to high-hardness water. So it was important to improve its scale inhibition performance by research on modified PASP, that was reported at home and abroad [5-7]. Several methods have since been developed to improve the corrosion and scale inhibition of PASP [8, 9]. The most promising method appeared to be the introduction of functional groups having scale inhibition effect (e.g., carboxylic acid, phosphonic acid and sulfonic acid) to the side chain of PASP through the ring-opening reaction by amine-group catalysis [10]. Polyaspartic acid derivative (ab. PASP-SEA-ASP) with a side chain aspartic acid and sulfonic acid group was synthesized in this paper. And the property of scale inhibition and corrosion inhibition of PASP-SEA-ASP were studied. The structure of polyaspartic acid derivative was characterized by means of FTIR. Calcium carbonate crystals in scale samples and corrosive test pieces were analyzed by means of SEM.

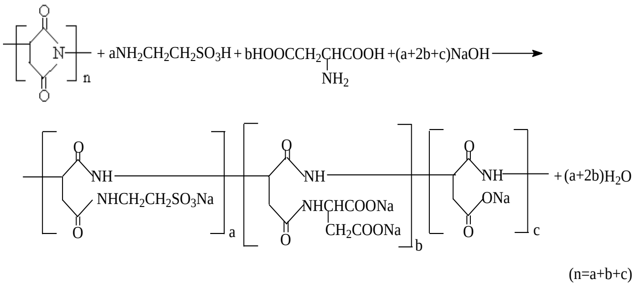
II. EXPERIMENTAL METHODS

A. Synthesis of Polysuccinimide



Polysuccinimide was synthesized by pyrocondensation of L-aspartic acid monomer (commercial product) under the condition of temperature 240^{O}C and reaction time 4 hours in an electric thermostatic drying oven.

B. Synthesis of polyaspartic acid derivative



Aspartic acid and 2-aminoethanesulfonic acid was dissolved respectively in 10% NaOH solution. Then water was added into polysuccinimide to form a suspension, and then aspartic acid, 2-aminoethanesulfonic acid and 10% NaOH solution was slowly dropped into the suspension. The mixture was stirred at 25^{O}C for 24 h, pH was kept at 8~9. Then be acidified, filtration, washing with absolute alcohol and drying. Finally a red-brown power of PASP-SEA-ASP was attained.

C. Measurement of the rate of static scale inhibition

Water sample is confecting water (containing calcium carbonate 400 mg/L). Heat 500 mL confecting water with an amount of PASP-SEA-ASP to 80^{O}C and then keep 80^{O}C to 10 hours. The content of calcium carbonate in the cooling and filtrating water was determined by EDTA titration. The rate of scale inhibition is calculated from formula (1).

$$\mathit{Rate\ of\ scale\ inhibition} = \frac{\rho_2 - \rho_0}{\rho_1 - \rho_0} \times 100\% \qquad (1)$$

Where ρ_2 is mass concentration of Ca^{2+} of water sample with PASP-SEA-ASP composite, mg/L; ρ_0 is mass concentration of Ca^{2+} of water sample without PASP-SEA-ASP composite, mg/L; ρ_1 is mass concentration of Ca^{2+} of preparing water sample, mg/L.

D. Measurement of the rate of corrosion inhibition

The corrosion inhibition performance of polyaspartic acid derivative was estimated by rotating hanging piece corrosion test. The main steps as follows: A 1600 mL solution with water treatment chemical is prepared in a beaker and the content of water treatment chemical is 100 mg/L. Put the beaker in a constant temperature bath and keep the temperature at 40^{O}C. Then hang test piece in solution and rotate at stated velocity. The test piece is taken out from solution after 72 h, then dipped in the solution of hydrochloric acid pickling for 3-5 min, washed with water, dipped in pure ethanol for 3 min, blot up with filter paper, and dried in dryer for 4 h. The rate of corrosion of water treatment chemical is calculated by formula (2).

$$X = \frac{8760 \times (W_0\text{-}W) \times 10}{A \times D \times T} \qquad (2)$$

Where W is the mass of the corrosive test piece, g; W_0 is the initial mass of the test piece, g; A is surface area of the test piece, cm^2; D is the density of test piece, g/cm^3; T is test time of test piece, h.

The rate of corrosion inhibition of water treatment chemical is calculated by formula (3).

$$\text{Rate of corrosion inhibition} = \frac{X_0\text{-}X_1}{X_0} \times 100\% \qquad (3)$$

Where X_0 is the rate of corrosion of the test piece without water treatment chemical, mm/a; X_1 is the rate of corrosion of the test piece with water treatment chemical, mm/a.

E. Preparation of scale sample

The rate of static scale inhibition of sample was measured at 80^{O}C. The solution was removed from the beaker at the end of experiment, and the scale attached to bottom and on wall of the beaker was dried at room temperature. The dried scale was then brushed away and conserved in a dryer.

III. RESULTS AND DISCUSSION

A. Characterization of polyaspartic acid derivative

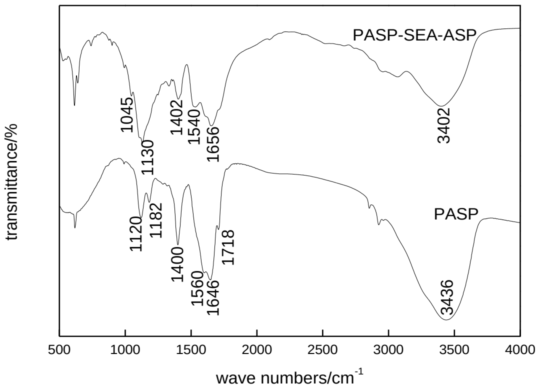


Figure 1. FT-IR spectrum of PASP-SEA-ASP

1045 cm^{-1} peak was absorption peak of $-SO_3Na$. PASP has not the absorption peak. 1130 cm^{-1} peak was absorption peak of C-N. This absorption peak of PASP-SEA-ASP was stronger than PASP. And 3402 cm^{-1} peak was absorption peak of N-H of amide. This absorption peak of PASP-SEA-ASP take place displacement compared with PASP. That showed PASP-SEA-ASP was prepared from PSI that was thermal condensation polymer of ASP, SEA and ASP.

B. Scale inhibition performance

TABLE I. RELATION BETWEEN DOSAGE OF PASP-SEA-ASP AND SCALE INHIBITION RATE

Dosage (mg/L)	2	4	6	8
Scale inhibition rate (%)	59.55	67.42	60.67	58.43

The results showed PASP-SEA-ASP was a good scale inhibitor, under Ca^{2+} 400 mg/L, HCO_3^- 800 mg/L and PASP-SEA-ASP composite 4 mg/L, the scale inhibition rate of PASP-SEA-ASP can reach 67.42%. The rate of static scale inhibition of water containing PASP-SEA-ASP composite decreases from 67.42% to 58.43% when the dosage of PASP-SEA-ASP from 4 mg/L to 8 mg/L. Its reason was sulfonic acid group was more increased than carboxylic acid group with the dosage of PASP-SEA-ASP was bigger. And sulfonic acid group possessed better dispersing performance than that of chelating Ca^{2+} ion. So its rate of scale inhibition was decreased.

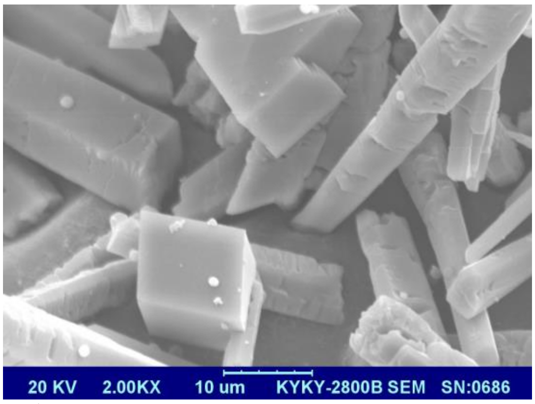
C. *Corrosion inhibition performance*

TABLE II. RESULTS OF ROTATION SPECIMEN METHOD

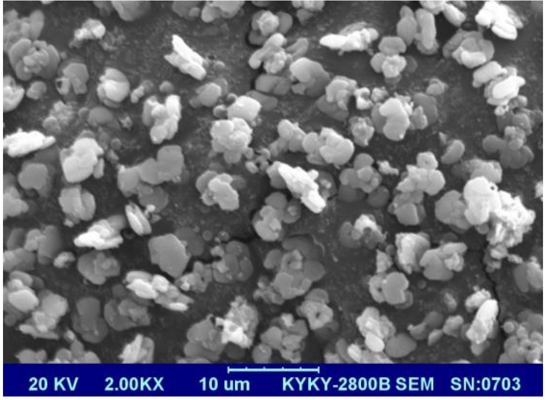
Chemical	**Lost mass of test piece (g)**	**Corrosion rate (mm/a)**	**Corrosion inhibition rate (%)**
Blank	0.03406	0.18853	/
PASP	0.01724	0.09543	49.38
PASP-SEA-ASP	0.01106	0.06122	67.53

It was found that polyaspartic acid derivative possessed good corrosion inhibition performance and the corrosion inhibition rate can reach 67.53%. The corrosion inhibition rate of polyaspartic acid derivative increased about 18% than polyaspartic acid in dynamic experiment.

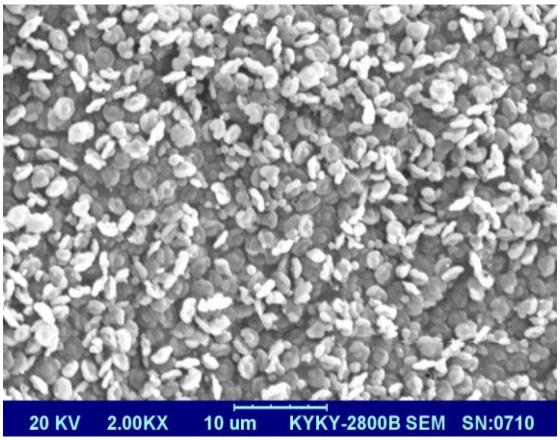
D. *Results of SEM*



（a）SEM photograph of $CaCO_3$ sample from blank solution



（b）SEM photograph of $CaCO_3$ sample from the solution with 4 mg/L PASP-SEA-ASP

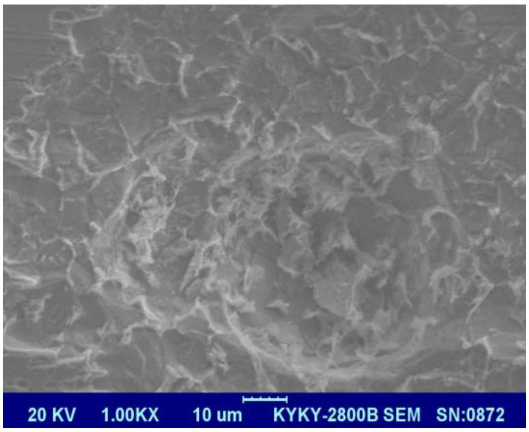


（C）SEM photograph of $CaCO_3$ sample from the solution with 8 mg/L PASP-SEA-ASP

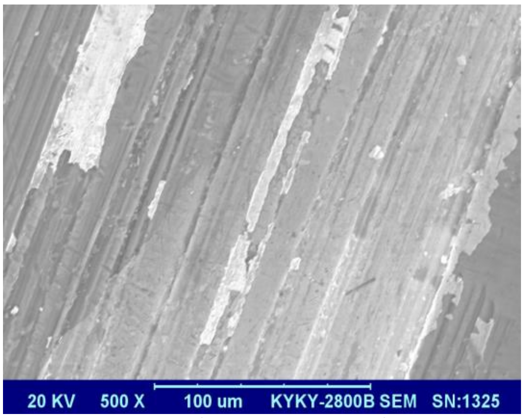
Figure 2. SEM photograph of $CaCO_3$ sample from the solution with PASP-SEA-ASP

SEM images of $CaCO_3$ scale samples are formed under different conditions (see Fig .2). Fig .2 (a) shows the most of $CaCO_3$ crystals are calcite in the scale samples from blank solution. Fig .2 (b) shows $CaCO_3$ crystal lattice is distorted completely bases on calcite after 4 mg/L PASP-SEA-ASP composite is added in water, which is vaterite, $CaCO_3$ crystal grain obviously less than $CaCO_3$ crystal grain of blank solution. Fig .2 (c) shows 8 mg/L PASP-SEA-ASP composite makes $CaCO_3$ crystal lattice be distorted completely in the scale samples and formed $CaCO_3$ crystal lattice are more finer. The results of experiments show that almost all calcite and aragonite can be transformed into vaterite by using PASP-SEA-ASP composite. This is because PASP-SEA-ASP not only forms steady complex with Ca^{2+} in water to decrease concentration of Ca^{2+} in aqueous solution and decrease probability of forming $CaCO_3$ deposition, but also makes action with Ca^{2+} of formed $CaCO_3$ crystal lattice to make face of crystal lattice form a double layer and bring static exclusion among crystal lattice to block collision among them and formation of bigger crystal and block collision between heat transfer face of metal and them and formation of scale.

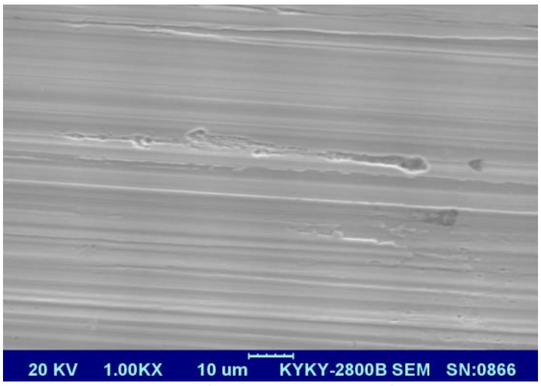
E. *Surface analysis of corrosive test piece*



(a) SEM photograph of corrosive test piece from blank solution



(b) SEM photograph of corrosive test piece from the solution with PASP



(c) SEM photograph of corrosive test piece from the solution with PASP-SEA-ASP

Figure 3. SEM photograph of corrosive test piece from the solution with water treatment chemical

If the test piece was immersed in blank solution, its surface was covered with pits of different sizes after experiment (Fig .3(a)), which showed that serious local corrosion occurred. The patterns of the sample immersed in PASP and PASP-SEA-ASP are showed in Fig .3(b) and (c). When immersed in solution with PASP, the surface had furfuraceous corrosion. While in solution with PASP-SEA-ASP, the sample surface had little pits. This indicated that the corrosion inhibition rate of polyaspartic acid derivative was higher than polyaspartic acid.

This was because polyaspartic acid and polyaspartic acid derivative could be adsorbed on the surface of metal. And they and metal could take place chemical reaction synchronously. And adsorption heat was higher and formed complex compound was steadier. Then a compact protective membrane of chemical adsorption was formed on the surface of test piece. This could prevent from corrosion effectively. In addition, nonpolar group that was –R was directional arranged on the surface of metal and hydrophobe membrane was formed, and that prevent from transfer of charge or matter that was relevant to corrosive reaction after polar group that is amino- and carboxyl are adsorbed on the surface of metal. Thus corrosion contaminant was supplanted and partitioned with surface of metal by corrosion inhibitor molecule. Then that slowed corrosion rate of metal down [8]. And carboxyl of molecular structure of polyaspartic acid derivative was more than polyaspartic acid, so the corrosion inhibition rate of polyaspartic acid derivative is higher than polyaspartic acid.

IV. CONCLUSIONS

Polyaspartic acid derivative (PASP-SEA-ASP) was prepared from polysuccinimide (PSI) that was thermal condensation polymer of aspartic acid (ASP), taurine (SEA) and ASP. It was a better scale inhibitor, under Ca^{2+} 400 mg/L, HCO_3^- 800 mg/L and polyaspartic acid derivative 4 mg/L, the scale inhibition rate of polyaspartic acid derivative can reach 67.42%. And it possessed better corrosion inhibition performance and the corrosion inhibition rate can reach 67.53%. The corrosion inhibition rate of polyaspartic acid derivative can increase by 18% than polyaspartic acid in dynamic experiment. Measuring results of SEM showed that polyaspartic acid derivative could distort calcium carbonate crystallite and made calcium carbonate crystallite more dispersive. Measured by SEM, the test piece was immersed in solution with polyaspartic acid derivative has little pits on its surface.

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