



Investigation of influence of low phosphorous co-polymer antiscalant on calcium sulfate dihydrate crystal morphologies



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HIGHLIGHTS

- A novel low phosphorus co-polymer with carboxyl and sulfonic groups was prepared.
- The co-polymer significantly inhibits formation of calcium sulfate dihydrate scale.
- The inhibition rate increases with increase of phosphorus content of co-polymer.
- The inhibition rate increases with decrease of viscosity average molecular weight.

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ABSTRACT

Increasing environmental concerns and discharge limitations have imposed additional challenges in industrial cooling water treatment. Increasing research efforts have been directed towards finding economical and environmentally friendly inhibitors. In this study, a novel inhibitor of low phosphorus co-polymer was prepared. The inhibition performance of the novel low phosphorus co-polymer as calcium sulfate dihydrate scale inhibitors, the influence of phosphorus content and viscosity weighted average molecular weight on inhibition were evaluated in simulated cooling water. The results indicate that the optimal preparation conditions of the novel low phosphorus co-polymer for inhibiting calcium sulfate dihydrate were 2.103 of sodium *p*-styrene sulfonate/maleic anhydride ratio, 0.26 of the ratio of hypophosphorous to monomer, and 0.57 of the ratio of hydrogen peroxide to hypophosphorous. The novel low phosphorus co-polymer strongly affected the calcium sulfate dihydrate scale formation, the scale inhibition rate was 94%, and phosphorus content and viscosity weighted average molecular weight also evidently influence the scale inhibition rate to calcium sulfate dihydrate. Scanning electronic microscopy and powder X-ray diffraction investigations reveal that the crystal structure of the calcium sulfate dihydrate is highly modified in the presence of the novel low phosphorus co-polymer.

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1. Introduction

The growth of calcium sulfate dihydrate scale from aqueous solutions in many industrial processes causes a serious problem, especially deposits on heat exchanger surfaces in industrial cooling water systems, boiler, oil and gas production, geothermal energy and distillation systems, leads to overheating, loss of system efficiency, unscheduled shutdown time, and ultimately heat exchanger failure. The calcium scaling from cooling water has been recognized as a potential impediment to the smooth operation of recirculating cooling water facilities owing to its reverse temperature-solubility characteristic precipitates [1,2]. Calcium sulfate is the dominated portion of calcium scales deposited in numerous industrial processes, such as distribution systems, boilers, oil well casings, cooling water systems, salt refineries, and other industrial production

processes. The chemical and mineralogical properties of calcium sulfate have been extensively studied [3–8]. Calcium sulfate may crystallize as calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, monoclinic, CSD), calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$, hexagonal, CSH) and calcium sulfate anhydrite (CaSO_4 , orthorhombic, CSA). The most calcium sulfate precipitation in recirculating cooling water systems is calcium sulfate dihydrate.

A number of methods have been proposed to retard or prevent calcium sulfate dihydrate scale formation on heat transfer surface. The conventional approach of calcium sulfate dihydrate scale inhibition in recirculating cooling water systems is the use of scale inhibitors (antiscalants). A considerable number of scale inhibitors of preventing or reducing the crystallization of calcium sulfate dihydrate have been investigated [1,6,9], such as phosphonates, organic phosphate esters, polyelectrolytes, and special types of polymer. As containing multi-

functional groups, the co-polymer scale inhibitor could prevent calcium sulfate dihydrate precipitation [10–13]. Polymers containing carboxyl groups were shown to be particularly effective as calcium sulfate crystal growth inhibitors [14], and the phosphono polymers could stabilize supersaturated calcium sulfate solutions and lengthen the induction period before the onset of calcium sulfate crystallization [9,15]. Due to the increasing likelihood of eutrophication in the receiving body of waters, the development of low phosphorus or non-phosphorus co-polymer as efficient scale inhibitor has attracted considerable attention [16–21].

In the work, the preparation of a novel low phosphorus co-polymer containing carboxyl groups and sulfonic groups was investigated. The inhibition performance of the novel low phosphorus co-polymer as calcium sulfate dihydrate scale inhibitors, the influence of phosphorus content and viscosity weighted average molecular weight on inhibition were evaluated in simulated cooling water. In addition, the effect of the low phosphorus co-polymer on interpreting crystal growth of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals through its adsorption was studied as well.

2. Experimental

2.1. Materials

The following reagents were acquired from commercial sources and were used without any further purification. Sodium p -styrene sulfonate (industrial grade) was afforded by Zibo Xingzhilian Chemical Co. (China). Hypophosphorous (Guaranteed reagent) was supplied by Nanjing Chemical Reagent Co. (China). Maleic anhydride, hydrogen peroxide, sodium hydroxide, calcium chloride, sodium sulfate and edetate disodium were analytical reagent grade, purchased from Sinopharm Chemical Reagent Beijing Co. (China). All solutions were prepared using deionized water.

2.2. Apparatus

The effect of the novel low phosphorus co-polymer on crystal formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was investigated with scanning electronic microscopy (SEM) and powder X-ray diffraction (XRD). The morphologies of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were examined by using a scanning electronic microscope (Quanta 200, USA). For XRD analysis, a diffractometer (XRD-6000, Japan) was used and the specimens were analyzed using Ni-filtered $\text{Cu-K}\alpha$ radiation generated at 40 kV and 30 mA at a scanning rate of $2^\circ/\text{min}$.

2.3. Synthesis of maleic acid and sodium p -styrenesulfonate co-polymer

The co-polymerization reaction was carried out in 250-mL flasks with a mechanical stirrer, a reflux condenser, a dropping funnel and a thermometer. 5.00 g maleic anhydride and 25 mL de-ionized water were mixed, stirring continuously at 50°C with nitrogen as protective gas. 10.515 g of sodium p -styrene sulfonate and desired amount of hypophosphorous acid were added respectively, and then the mixture was heated to the reaction temperature. In fixed temperature and stirring conditions, the desired amount of hydrogen peroxide was added drop by drop in a certain time and continued to react for a desired time. Finally the pH value of solution was adjusted to 6–7 by adding 20% NaOH solution.

2.4. Measure of the intrinsic viscosity of the co-polymer

The novel low phosphorus co-polymer samples were precipitated (not adjusted pH) and purified with ethanol.

The intrinsic viscosity $[\eta]$ of the co-polymer ($0.005\text{ g}\cdot\text{mL}^{-1}$) was measured in sodium thiocyanate aqueous solution ($0.15\text{ mol}\cdot\text{L}^{-1}$) with an Ubbelohde viscometer thermostated at $25 \pm 0.1^\circ\text{C}$, and

the viscosity weighted average molecular weight was calculated by Mark–Houwink empirical equation [22]:

$$[\eta] = KM^\alpha$$

where in:

$[\eta]$	is intrinsic viscosity
K	is a Mark–Houwink constant. Here $7.65 \times 10^{-6}\text{ mL}\cdot\text{g}^{-1}$ was adopted
α	is the other Mark–Houwink constant. Here 0.924 was adopted
M	is molecular weight

2.5. Inhibit calcium sulfate dihydrate scale test

To study the inhibitory effects of the novel low phosphorus co-polymer to calcium sulfate dihydrate scale we utilized the inhibition experiments. The inhibition tests were carried with artificial water which was prepared by first dissolving 5.0973 g CaCl_2 and desired amount of the novel low phosphorus co-polymer in 1000 mL pyrex glass vessel containing 500 mL deionized water, then 500 mL deionized water dissolved with 6.5239 g Na_2SO_4 was added. The initial total concentrations of Ca^{2+} ($C_{\text{Ca},i}$) and SO_4^{2-} ($C_{\text{SO}_4,i}$) were $4.59 \times 10^{-2}\text{ mol}\cdot\text{L}^{-1}$. After intensive mixing, the artificial water was concentrated heating at 80°C to approximately 800 mL.

The concentrations of soluble calcium ions in different solutions were analyzed using a standard solution of EDTA. The inhibition efficiency φ was defined as:

$$\varphi = \frac{\rho_1(\text{Ca}^{2+}) - \rho_2(\text{Ca}^{2+})}{\rho_0(\text{Ca}^{2+}) - \rho_2(\text{Ca}^{2+})} \times 100\%$$

where $\rho_0(\text{Ca}^{2+})$ was the total concentrations of Ca^{2+} ($\text{mg}\cdot\text{L}^{-1}$), $\rho_1(\text{Ca}^{2+})$ was the concentrations of Ca^{2+} ($\text{mg}\cdot\text{L}^{-1}$) in the presence of the novel low phosphorus co-polymer inhibitor, and $\rho_2(\text{Ca}^{2+})$ was the concentrations of Ca^{2+} ($\text{mg}\cdot\text{L}^{-1}$) in the absence of the novel low phosphorus co-polymer inhibitor. The morphologies of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precipitates were examined by SEM and XRD analyses.

3. Results and discussion

3.1. The calcium sulfate dihydrate inhibition of the novel low phosphorus co-polymer

The effect of the novel low phosphorus co-polymer as an antiscaling agent for calcium sulfate dihydrate was shown in Fig. 1. A series of 1000 mL artificial cooling water with different dosages of the novel low phosphorus co-polymer, that was prepared under optimum conditions, ranging from 4 to $20\text{ mg}\cdot\text{L}^{-1}$ were heated at 80°C to approximately 800 mL, respectively. Fig. 1 illustrates the ability of the novel low phosphorus co-polymer under identical conditions, it is seen that the calcium sulfate dihydrate inhibition rate is greatly increased by increasing the co-polymer concentration. When the co-polymer concentration increased, the calcium sulfate dihydrate scale inhibition rate enlarged correspondingly. When the concentration of the novel low phosphorus co-polymer increases from 4 to $8\text{ mg}\cdot\text{L}^{-1}$, the inhibition rate of calcium sulfate dihydrate increases suddenly, where the scale inhibition rate result is 20% at $4\text{ mg}\cdot\text{L}^{-1}$, but 86.4% for $8\text{ mg}\cdot\text{L}^{-1}$, and the curve increases very slowly when the concentrations increase from 8 to $20\text{ mg}\cdot\text{L}^{-1}$, where it reaches 86.4% at $16\text{ mg}\cdot\text{L}^{-1}$, and 96.8% for $20\text{ mg}\cdot\text{L}^{-1}$. The $14\text{ mg}\cdot\text{L}^{-1}$ was

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