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Calcium carbonate inhibition by a phosphonate-terminated poly(maleic-co-sulfonate) polymeric inhibitor

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ABSTRACT

The precipitation of calcium carbonate scale on heat transfer surfaces widely occurs in numerous industrial processes. For the control of calcium carbonate scale and in response to environmental guidelines, the new low phosphonic copolymer was prepared through reaction of maleic anhydride with sodium *p*-styrene sulfonate in water with redox system of hypophosphorous and hydrogen peroxide as initiator. The anti-scale property of the low phosphonic copolymer towards $CaCO_3$ in the artificial cooling water was studied through static scale inhibition tests, and the effect on formation of $CaCO_3$ was investigated with combination of scanning electronic microscopy (SEM), X-ray powder diffraction (XRD) analysis and Fourier transform infrared spectrometer, respectively. The results showed that the low phosphonic copolymer was excellent calcium carbonate scale inhibitor in artificial cooling water. The crystallization of $CaCO_3$ in the absence of inhibitor was rhombohedral calcite crystal, whereas a mixture of calcite with vaterite crystals was found in the presence of the low phosphonic copolymer. For actions of carboxyl and phosphonic acid groups, the calcite was inhibited and the metastable vaterite was stabilized in the presence of the low phosphonic copolymer during the $CaCO_3$ formation process.

1. Introduction

The precipitation of mineral scales on heat transfer surfaces widely occurs in numerous industrial processes. Deposits formation may cause severe corrosion and deteriorate conditions of the heat exchange. Calcium carbonate is the predominant component of scales deposited from natural water, especially in cooling water systems, owing to its inverse temperature–solubility characteristics.

The most common and effective scale control method is the use of scale inhibitors. Copolymer has been used satisfactorily as a specific scale inhibitor in the circulating cooling water systems, because of its strong complexation of functional groups and superior dispersion characteristic of macromolecule. The low phosphonic copolymer was synthesized with water as solvent and redox system of hypophosphorous and hydrogen peroxide as initiator, through reaction of maleic anhydride(MA) with sodium *p*-styrene sulfonate(SS). The optimal synthetics conditions were that the ratio of SS:MA was 0.8:1.0 (mole ratio); dosage of hypophosphorous was 16% of total SS and MA (mole number); hydrogen peroxide was 1.2 times of hypophosphorous (mole number); reaction temperature was 65 °C; and reaction time was 90 min.

The elemental composition analysis by EDX showed that phosphorus content of the low phosphonic copolymer was less than 3.6% (mass percentage), so the low phosphonic copolymer is a new environmentally safe cooling water treatment agent. The viscosity-average molecular weight of the copolymer was 1.7×10^4. Terminal phosphoro-to-carbon bond in the copolymer molecular structure was identified by ^{31}P NMR spectra, the main chain structure of the copolymer was alternating structure units of styrene sulfonic acid and maleic acid which was identified by ^{13}C NMR spectra. The polar groups of carboxyl($1719\ cm^{-1}$), sulfo-group($1038\ cm^{-1}$, $1181\ cm^{-1}$) and phosphino-group($776\ cm^{-1}$, $1006\ cm^{-1}$, $1126\ cm^{-1}$) on the side chains were notarized by IR. The molecular structure of low phosphonic copolymer is presented in Fig. 1.

In the present work, the anti-scale property of the low phosphonic copolymer towards $CaCO_3$ in the artificial cooling water was studied through static scale inhibition tests, and the effect on the formation of calcium carbonate scale was investigated with scanning electronic microscopy (SEM), X-ray powder diffraction (XRD) analysis and Fourier transform infrared spectrometer, respectively.

2. Experimental

The ability of the low phosphonic copolymer to inhibit calcium carbonate scale was compared with that of the free-inhibitor in flask tests. The experimental procedures used in this study were described in reference [1]. Calcium carbonate precipitation and inhibition were studied in artificial cooling water which was prepared by dissolving a certain quantity of $CaCl_2$ and $NaHCO_3$ in deionized water. Two concentrations of Ca^{2+} and HCO_3^- were $250\ mg\cdot L^{-1}$. The artificial cooling water containing different quantities of the low phosphonic

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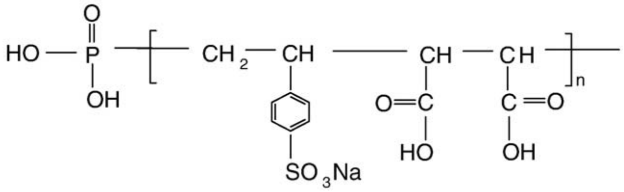

Fig. 1. Diagram of the molecular structure of the low phosphonic copolymer.

copolymer was thermostated at 80 °C for 10 h. Calcium chloride and sodium bicarbonate used to prepare the scaling test solution were of analytical reagent grade. The low phosphonic copolymer had been synthesized in the laboratory.

Solution was analyzed after every set of experiments with respect to soluble calcium ions using a standard solution of EDTA according to standard methods [1]. The inhibition efficiency φ was defined as

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

where $\rho_0(\mathrm{Ca}^{2+})$ was the total concentrations of $\mathrm{Ca}^{2+}(\mathrm{mg \cdot L^{-1}})$, $\rho_1(\mathrm{Ca}^{2+})$ was the concentrations of $\mathrm{Ca}^{2+}(\mathrm{mg \cdot L^{-1}})$ in the absence of the low phosphonic copolymer, $\rho_2(\mathrm{Ca}^{2+})$ was the concentrations of $\mathrm{Ca}^{2+}(\mathrm{mg \cdot L^{-1}})$ in the presence of the low phosphonic copolymer.

The morphologies of $CaCO_3$ were examined by SEM on a scanning electronic microscope (Quanta 200). Precipitated phases were identified by XRD on an X-ray powder diffractometer (XRD-600 using Ni-filtered Cu$K\alpha$ radiation), and an FTIR spectrophotometer (Tensor 27 using KBr pellets).

3. Results and discussion

3.1. Anti-scale property of the low phosphonic copolymer towards $CaCO_3$

The effect of the low phosphonic copolymer as an anti-scale agent for calcium carbonate is shown in Fig. 2. Different quantities of the low phosphonic copolymer ranging from 2 ppm to 20 ppm were heated at 80 °C for 10 h, respectively. Fig. 2 illustrates the ability of the low phosphonic copolymer under identical conditions. When the copolymer concentration changes, the inhibition effect also changes correspondingly, scale inhibition effect increases with increasing the copolymer concentration. There is a sudden increase of scale inhibition as the concentration increases from 2 ppm to 8 ppm, which reaches 26.5% using 2 ppm, 90.3% for 8 ppm, and moderately higher by further increasing the concentrations from 8 ppm to 20 ppm, which reaches 98.2% using 16 ppm and 98.4% for 20 ppm.

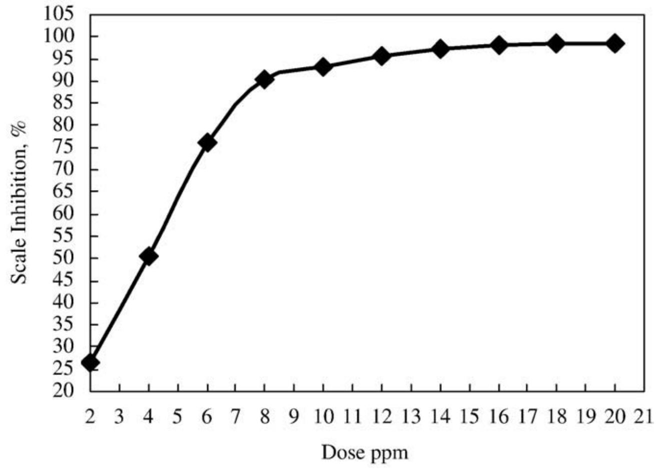

Fig. 2. Influence of the inhibitor concentrations on the inhibition efficiency.

3.2. Characterization of scales

Fig. 3 shows the SEM micrographs of $CaCO_3$ precipitate formed in artificial cooling water. In the absence of the low phosphonic copolymer the precipitates which were deposited had the form as shown in Fig. 3a. They were essentially well-regulated orthorhombic calcite particles with average particle size about 10 µm. The SEM micrographs of particles on addition of 8 ppm of the low phosphonic copolymer are shown in Fig. 3b. A very obvious change was noted at the distribution, size and morphology of the $CaCO_3$ precipitate, $CaCO_3$ lost its sharp edges, form was distorted and the size has increased to 25–30 µm larger than those deposited in uninhibited solution.

It is generally accepted that the inhibition of scale formation is influenced by both the location of the adsorbed inhibitor at the crystal surface and the extent of chemical bonding with the surface [2]. The more effective the inhibitor is, the higher the surface binding capability. Organic phosphonic and carboxyl can strongly adsorb onto a $CaCO_3$ crystalline substrate owing to the high chelating ability of the $–P(O)(OH)_2$ group and $–COO^-$ group [3–6].The low phosphonic copolymer contains both carboxyl and phosphonic groups in one molecule, therefore, its surface-binding capability is stronger and

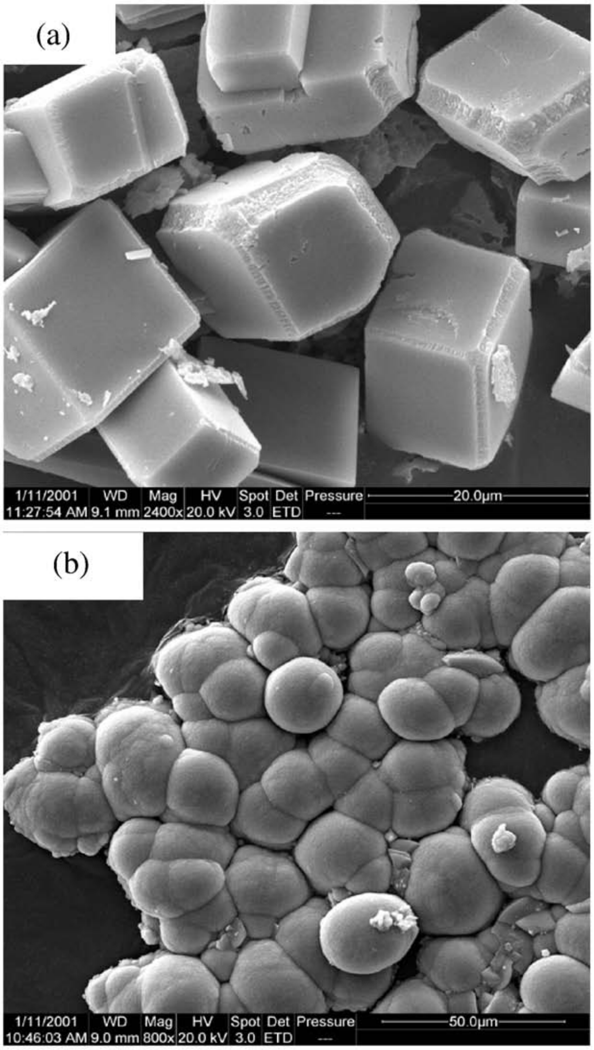

Fig. 3. SEM micrographs of $CaCO_3$ precipitates. (a) In the absence of the low phosphonic copolymer and (b) in the presence of 8 ppm the low phosphonic copolymer.