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Research paper

Preparation and application of copolymer modified with the palygorskite as inhibitor for calcium carbonate scale

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ABSTRACT

The scale inhibitor copolymer modified with palygorskite was prepared from maleic anhydride, styrene sulfonic sodium and palygorskite. The conditions of preparing scale inhibitor were optimized. The structure and morphology of the copolymer were characterized by FT-IR, SEM and XRD. Using the static experiment method, the influences of copolymer concentration, temperature, time, and Ca^{2+} concentration of the system on the inhibition efficiency were investigated. The experimental results showed that the scale inhibitor copolymer modified with palygorskite had an excellent efficiency of scale inhibition, and nearly 98.97% of scale inhibition efficiency for $CaCO_3$ was obtained. The prepared scale inhibitor could be used in the system of high temperature and high hardness water.

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 (Wang et al., 2009). Inorganic scale formation in the wellbore, surface facilities and near wellbore formation is a common cause of production loss in most matured fields (Kumar et al., 2010). Calcium carbonate is the predominant component of scales deposited from natural water, especially in cooling water systems, owing to its inverse temperature–solubility characteristics (Wang et al., 2009). Scale can deposit on almost any surface so that once a scale layer is first formed it will continue to get thicker unless treated (Kelland, 2011). Calcium carbonate formation rates are controlled by many factors such as calcium concentration and supersaturation, temperature, pH, CO_2, water composition, water hardness, pressure or/and nature of the substrate in contact with water (Setta and Neville, 2011).

The most practical and economical method to combat this problem is the use of chemical scale inhibitors (Tantayakom et al., 2005). Because of their strong scale inhibition performance and dispersing capability, they have been used satisfactorily in the circulating cooling water systems. Phosphorus scale inhibitors are usually used in China, such as phosphonates, organic phosphorus-containing copolymers. These phosphorus compounds are eventually let out with wastewater, resulting in environmental pollution and ecological imbalance in water (Zhou et al., 2011). However, the phosphonates will cause eutrophication of water; phosphonate scale inhibitors are generally mixed with other additives to avoid corrosion or bacterial fouling. So, high levels of phosphonates are becoming increasingly restricted in terms of release to the environment (Kumar et al., 2010).

In recent year, the no phosphorus copolymers have attracted great interests, both in industry and in academia. Under the pressure of worsening global ecological and environmental problems, the concept of “Green Chemistry” was proposed and green scale inhibitors became a focus of water treatment technology (Guo et al., 2012). More recently,palygorskite has already been used in the field of environmental protection because of its large specific surface area and low cost, which has made it an important material in the treatment of organic wastewater. Acid activation is a usual method employed for improving the surface properties of clay minerals (Woumfo et al., 2007). This chemical treatment allows optimizing the adsorption capacity of some clay in different fields, like in water pollution (Amari et al., 2010; Frini-Srasra and Srasra, 2010). Moreover, it is cheaper and can be used as a green inhibitor like other materials which have been used previously to save our environment (Suharso et al., 2011).

In this work, the scale inhibitor copolymer modified with the was synthesized from maleic anhydride (MA), styrene sulfonic sodium (SSS) and palygorskite (Pal) by the free-radical polymerization. The effects of reaction time, content of monomer, content of initiator, reaction temperature to inhibit calcium carbonate scale were studied. Using the static experiment method, the scale inhibition efficiency for $CaCO_3$ scale was investigated. To the best our knowledge, this is the first time that calcium carbonate scale inhibition applications of scale inhibitor copolymer modified with Pal are reported.

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2. Experimental

2.1. Materials

Pal, MA, SSS and ammonium persulfate were supplied by Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China). All chemicals are reagent grade and were used as received.

2.2. Preparation of scale inhibitor copolymer modified with Pal

Pal was carried out by acid treatment and the process was as the following steps. Pal (10 g) was deposed in hydrochloric acid solution (100 mL, 2 mol/L) in a flask, and stirred magnetically for 30 min at 30 °C. Then, the solution was vibrated with the aid of ultrasonic instrument for 10 min at room temperature. After removing the supernatant, the residue was centrifuged and washed with distilled water several times until pH = 7 and drying under vacuum at 105 °C. After grinding, the acid activated palygorskite (HPal) solid was obtained and stored in a desiccator.

A certain amount of HPal was dissolved in 15 mL of water solution in a four-necked flask encircled with water-bath at 80 °C and the solution was stirred for about 2 h. Then, SSS, MA and initiator ammonium persulfate mixed solution was dropped slowly, and the reaction was left for 5 h under slow agitation. The scale inhibitor copolymer (HPal–SSS–MA) was obtained by evaporation–crystallization process. The synthetic route of scale inhibitor copolymer was shown in Fig. 1.

2.3. Evaluation of scale inhibitor by static scale inhibition method

Static scale inhibition tests were conducted according to the China National Standard method (GB/T 16632-2008) to evaluate the scale inhibition efficiency of the prepared HPal–SSS–MA copolymer against $CaCO_3$ scale. The scale inhibitor solution was dropped into $CaC1_2$ solution in a 250 mL volumetric flask, followed by adding borate buffer solution and $NaHCO_3$ solution to the flask. The mixture solution was diluted to 250 mL with distilled water and stirred to ensure complete mixing, then, transferred into an Erlenmeyer flask and immerged into water-bath at 70 °C for 10 h. In addition, a blank experiment without scale inhibitor added was made as a reference. The ultimate inhibition efficiency (φ) was obtained by the formula as below:

$$\varphi = \frac{V_2 - V_0}{V_1 - V_0} \times 100\% \tag{1}$$

where V_1 was the ethylene diamine-*N,N*-tetraacetic acid (EDTA) volume consumed by all calcium cations in the solution; V_0 was the EDTA volume consumed by certain calcium cations without the scale inhibitor in the solution, while V_2 was the EDTA volume consumed by certain calcium cations with the scale inhibitor in the solution.

2.4. Characterization

FT-IR spectra were carried out on a FT-IR spectrometer (AVATAR 360, Nicolet, Madison, USA) at room temperature using KBr pellets. FT-IR spectra were obtained at a 2 cm^{-1} resolution and recorded in the region of 4000–400 cm^{-1}. The samples and background scanning times were both 32. X-ray diffraction (XRD) measurements were recorded using a Rigaku D/MAX-R with a copper target at 40 kV and 40 mA. The power samples were spread on a sample holder and the corresponding data were collected from 5–80° at a scanning rate of 1°/min. The fracture surface of the sample was investigated with a 15-kV accelerating voltage with a Scanning Electron Microscope (SEM) (S-4800, Hitachi Corp., Tokyo, Japan). Powder samples were dispersed in ethanol in an ultrasonic bath for 10 min before the SEM examination.

3. Results and discussions

3.1. Optimum condition of preparing scale inhibitor

3.1.1. Effect of HPal content

The effect of the HPal content on the calcium carbonate scale inhibition efficiency was obtained and the result was listed in Table 1. As can

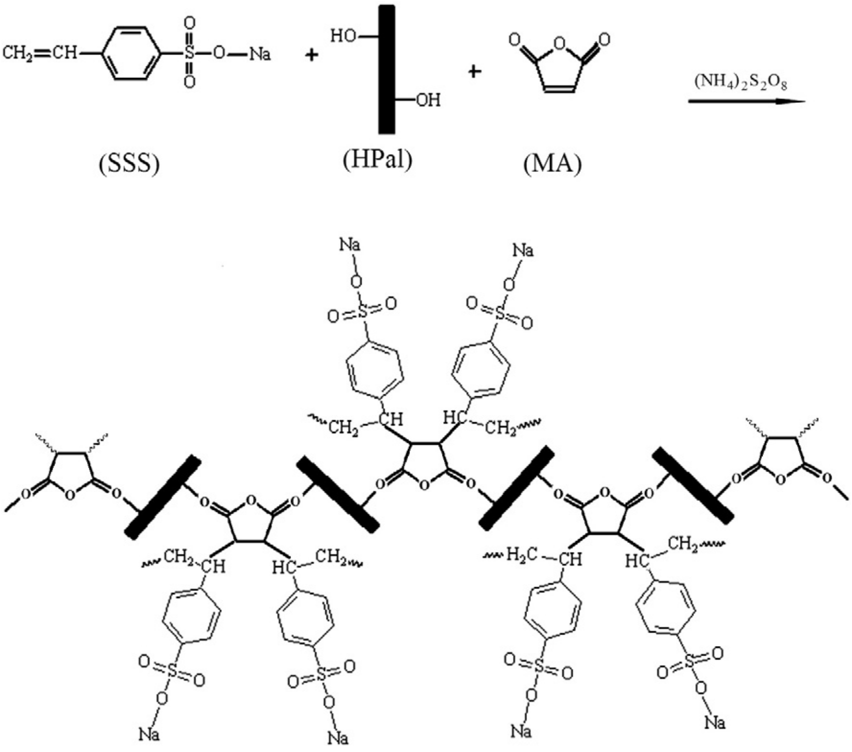

Fig. 1. The synthetic route of scale inhibitor copolymer.