



Inhibition of calcium sulfate scale by poly (citric acid)



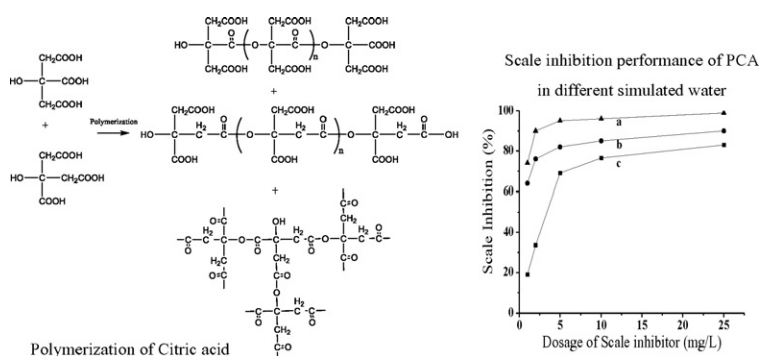
Yuzeng Zhao *, Lingling Jia, Kuaiying Liu, Pan Gao, Honghua Ge, Lijun Fu

Shanghai Engineering Research Center of Heat-exchange System and Energy Saving, Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai University of Electric Power, Shanghai 200090, People's Republic of China

HIGHLIGHTS

- Condensation polymerization of citric acid successfully prepared Poly (citric acid).
- Poly (citric acid) has excellent inhibition performance for CaSO₄ scale.
- Poly (citric acid) decreases deposit of CaSO₄ crystals in simulated scaling water.
- Poly (citric acid) can distort CaSO₄ crystal polymorphs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 December 2015
 Received in revised form 6 April 2016
 Accepted 7 April 2016
 Available online 22 April 2016

Keywords:

Scale inhibitor
 Poly (citric acid)
 Calcium sulfate

ABSTRACT

Condensation polymerization of citric acid successfully prepared Poly (citric acid). The polymerization product has characterized by FTIR and UV spectroscopy. The polymerization has confirmed to perform well and there are suspended carboxylic groups on the polymer molecules. Inhibition performance of new obtained poly (citric acid) for CaSO₄ scale has evaluated by static scale inhibition method. When the dosage of polymer scale inhibitor is 2.5 mg/L in initial simulated scaling aqueous solution in which the ion concentrations of Ca²⁺ and SO₄²⁻ are both 2040 mg/L, the scale inhibition rate exceeds to 90%. When the dosage of polymer scale inhibitor is 25 mg/L, the scale inhibition rate is up to 98.8%. All of the results indicate that poly (citric acid) increase the Ca²⁺ ion concentration in heated simulated scaling water and decrease the deposit of CaSO₄ crystals. The CaSO₄ crystals collected from simulated scaling water observed by SEM and characterized by FTIR and XRD. The results illustrate that the polymer inhibitor evidently affects the procedure of scale crystal growing. Poly (citric acid) might absorb on the surface of CaSO₄ scale crystals and distort the CaSO₄ scale crystal polymorphs. Therefore, poly (citric acid) could use as a kind of potential CaSO₄ scale inhibitor.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Research and Development of environmental friendly calcium scale inhibitor is very important to cycle cooling water system [1], reverse osmosis desalting water system [2–5], petroleum well pipeline [6–8] and flue gas desulfurization system [9,10]. In these systems, the calcium scales usually formed and attached to the surface of equipment [11]

and are difficult to clean up. It would be significantly harmful to the equipment of these systems, such as the scale might lead to equipment corrosion and reduce heat transfer efficiency or increases the fluid flow resistance, which will cause great economic losses. Therefore, scale inhibitors used in those systems to prevent or reduce the formation of calcium scale. There are some small molecular organic phosphine compounds or phosphorus containing oligomer used as efficient scale inhibitors, but compounds containing phosphorus are harmful to the environment. Consequently, it is necessary to develop scale inhibitors without phosphorus.

* Corresponding author.

E-mail address: zhaoyuzeng@shiep.edu.cn (Y. Zhao).

Some water-soluble polymers contained carboxylic groups used as novel scale inhibitors because they are mostly non-toxicity and wide applicability. There were many valuable and significant researches on poly (acrylic acid) [12,13], poly (aspartic acid) [14,15], poly (maleic anhydride) [16–20], poly (epoxy succinic acid) [14,21,22], botanical polysaccharide [23], chitosan and their derivatives [24], which were used as polymer scale inhibitors. However, those polymer scale inhibitors are expensive or difficult to be massively prepared, even some of which still have relatively low scale inhibition ability in some conditions. Therefore, it is still valuable to research and develop a kind of novel environmentally friendly, cheap and efficient polymer scale inhibitor.

Poly (citric acid) (PCA) is potential environment-friendly polymer scale inhibitor, which could be prepared from citric acid (CA). Citric acid is an environment-friendly monomer since it derived from natural resources and often used as additive in food. Citric acid has obviously chelating ability for metal ions to change the morphology during the formation of crystal since there are three carboxyl groups and one hydroxyl group in a citric acid molecule, which had made citric acid to be used as additive in nano-materials synthesis. For examples, citric acid could increase the solubility of aluminum oxyhydroxides in aqueous solutions [25], various distinct morphologies ZnO could obtain by simply changing the concentration of citric acid or citrate additive [26] and citrate additive also evidently affected the formation process of silver nanoplates [27]. It worked well apparently when citric acid used as additive in the transformation of calcium sulfate (CaSO_4) hemihydrate to gypsum [28]. Citrate has used as scale inhibitor for calcium carbonate (CaCO_3) [29–32] since it has absorption ability on calcium carbonate crystal that can prevent crystal particles growing. Citric acid is not an efficient scale inhibitor for calcium sulfate in water system. As it is well known, poly (aspartic acid) or poly (acrylic acid) has better scale inhibition performance than its small molecule monomer, i.e. aspartic acid or acrylic acid. Boeckh [33] discovered that PCA improved incrustation-inhibiting effect and added PCA into detergents and cleaners to clean the ash on clothes. Here, we prepared PCA and estimated its scale inhibition performance for calcium sulfate. In addition, poly (citric acid) is also a typical environmentally friendly polymer. Poly (citric acid) is one sort of polyester contains ester bonds in the polymer molecule skeleton formed through the reaction of carboxyl and hydroxyl groups in different citric acid molecules. The polyesters are easily biodegradable since the ester bonds can hydrolyzed into carboxyl and hydroxyl groups and the hydrolysis product is citric acid [34].

In the paper, condensation polymerization of citric acid successfully prepared PCA and PCA scale inhibition performance for calcium sulfate estimated by static scale inhibition method. The crystals of calcium sulfate collected from simulated scaling water observed and characterized by scanning electron microscope (SEM), Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD).

2. Experimental

2.1. Materials

Citric acid (the First Reagent Factory, Shanghai), tetrahydrofuran (Shanghai Aibi Chemistry Preparation Co. Ltd., Shanghai), sulfuric acid (Shanghai Experiment Reagent Co. Ltd., Shanghai) and other chemical reagents are all analytical reagents (AR) and are used directly without purify treatment.

2.2. Synthesis of PCA

A typical synthesis process described as follow: Citric acid (4.0 g) placed in a round flask and dissolved in 20 mL tetrahydrofuran (THF). Then 3.0 mL sulfuric acid dripped into the flask in an hour with electromagnetic stirring. The reaction solution maintained 60 °C with electromagnetic stirring for 6 h. The reaction solution in the flask was adjusted to neutral ($\text{pH} \approx 6\text{--}7$) by 1 mol/L sodium hydroxide solution

after it was cooled to room temperature. The neutral solution saturated with sodium sulfate powder. Then poured the solution into a separating funnel and let the solution stand to stratify into two layers. The upper layer is THF solution in which contains most polymers. The bottom layer is saturated sodium sulfate aqueous solution. The THF solution moved from the separating funnel and separated by vacuum distillation in a rotary evaporator. The polymer product dried in vacuum at 50 °C for 24 h.

2.3. Characterization of PCA

2.3.1. Fourier transforms infrared (FTIR) spectroscopy

The polymer pressed into tablet samples with potassium bromide (KBr) powder, and the samples characterized by a FTIR-8400S spectrometer (Shimadzu Co. Ltd., Japan).

2.3.2. Ultraviolet visible (UV) spectra

1.0 g/L monomer and polymer aqueous solutions were prepared and scanned UV spectra on a UV-2007 spectrometer (Shimadzu Co. Ltd., Japan) with wavelength from 190 to 900 nm by using Deion water as reference.

2.4. Evaluation of PCA scale inhibition performance by static scale inhibition method

The prepared polymers estimated the scale inhibition performance by the static scale inhibition test referring to literature [35], the national standard of the People's Republic of China (GB/T16632–2008). The initial test solution contained 2040 mg/L Ca^{2+} (Made by CaCl_2) and 2040 mg/L SO_4^{2-} (Made by Na_2SO_4). The Ca^{2+} concentration in blank solution without PCA scale inhibitor was directly titrated by 0.05 mol/L sodium ethylene diamine tetracetate (EDTA) standard solution by using eriochrome black T as indicator. The mixed solutions without or with different concentrations of PCA scale inhibitor were kept at 80 °C for 10 h, then the Ca^{2+} concentrations of all of those solutions were titrated by the same EDTA standard solution mentioned above. The scale inhibition rate calculated by the following formula:

$$\text{Scale inhibition rate (\%)} = (V_0 - V) / (V_0 - V_1) \times 100\%$$

Where, V_0 is the consumption volume of EDTA standard solution to titrate the blank solution without PCA scale inhibitor. V is the consumption volume of EDTA standard solution to titrate the mixed solution containing PCA scale inhibitor and kept at 80 °C for 10 h. V_1 is the consumption volume of EDTA standard solution to titrate the mixed solution without scale inhibitor and kept at 80 °C for 10 h.

2.5. Characterization of calcium sulfate scales

2.5.1. Scanning electron microscope (SEM)

The dried CaSO_4 crystals obtained by filtering the mixed solutions in the static scale inhibition tests mentioned above respectively observed by SEM (SU150 Hitachi Co. Ltd.) at an accelerating voltage of 15 kV after vacuum sputtering gold to the crystal particle surface.

2.5.2. X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) patterns of CaSO_4 crystal recorded on a D8 Advance XRD diffractometer (Bruker Co., Germany) with $\text{Cu K}\alpha$ radiation.

3. Results and discussion

3.1. Synthesis of PCA

The PCA molecule prepared by citric acid (CA) condensation polymerization is likely hyperbranched structure in theory speculation.

Download English Version:

<https://daneshyari.com/en/article/622770>

Download Persian Version:

<https://daneshyari.com/article/622770>

[Daneshyari.com](https://daneshyari.com)