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Evaluation of β-cyclodextrin–polyethylene glycol as green scale inhibitors for produced-water in shale gas well

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HIGHLIGHTS

- The β-CD–chitosan is an effective green inhibitor for calcium carbonate scale.
- The inhibitor dosage, bath time and Ca^{2+} concentration influence the efficiency.
- The SEM, XRD and TGA analyses support the static experiments.
- Could be used for the produced-water in shale gas well

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ABSTRACT

Reducing the formation of inorganic scales in reuse of shale gas extraction produced-water presents a challenge for desalination systems. The effects of polyethylene glycol modified natural β-cyclodextrin as an economical and environmentally friendly inhibitor have been investigated by the static experiments, scanning electron microscopy (SEM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The experimental results revealed that β-CD–PEG (polyethylene glycol modified β-cyclodextrin) achieved the maximum scaling inhibition efficiency of 89.1%, at the 180 mg/L inhibitor, 200 mg/L Ca^{2+} in the thermostat water bath at 40 °C for 6 h. The results of SEM and XRD studies revealed that both the morphology and aggregation of calcium carbonate crystals had been changed, when the inhibitor was added. Moreover, the TGA further confirmed the scaling mechanism of the copolymer. When the treated water and formation water were mixed together, during the compatibility tests, the mixture was clear. Therefore, the green inhibitor could be applied to prevent the buildup of calcium carbonate for the oilfield flow back water.

1. Introduction

As shale gas exploration is expected to become global, many countries take active exploration, such as the U.S., China, Germany, Poland, Australia, and New Zealand. At the same time, public concern of water usage is increasing for the shale gas basins [1] because hydraulic fracturing has increased and expanded with its application to horizontal drilling [2]. The Environmental Protection Agency (EPA) estimates that 7.6–19 million liters of water are needed in a single shale gas well to drill a horizontal hydraulically fractured well depending on the depth, horizontal distance, and fractured number of times [3]. Besides, 10–70% of the wastewater produced from hydraulic fracturing is subsequently recovered as flow back water [4,5]. The impaired water stream contains different potentially hazardous inorganic ingredients with extremely high concentrations, of which the constituents (e.g., calcium, barium, sulfate, and carbonate) can potentially form stable carbonate and sulfate precipitates in the wellbore (e.g., $CaCO_3$, $BaSO_4$), making the effective inner diameters of pipelines smaller and eventually causing the reduction of gas production [6–8].

The most common and effective method of scale controlling is the use of chemical additives as scale inhibitors which can retard or prevent scale formation [9–11]. At present, Amino Trimethylene Phosphonic Acid (ATMP) and 2-Phosphonobutane-1,2,4-Tricarboxylic Acid (PBTCA) are well known scale inhibitors in shale gas field [12]. Although the nitrogen, and phosphorus containing scale inhibitors are highly efficient, their use is limited because these compounds are nutrients for algae, which has the potential to ruin the environment. Thus, the new generation of environmental regulation requires the environmentally-friendly "green" additives with natural polymers [13].

β-Cyclodextrin is a kind of starch that consists of seven glucose units linked by a-1,4 glucosidic bonds which has a special structure of conical cavity with hydrophilic external cavity and oleophilic internal cavity

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[14,15]. The special torus-shaped cavity can incorporate organic and inorganic molecules of appropriate size as the guest including cations [16]. The CDs are non-toxic and can play a role in applications such as drug carrier [17], food [18], cosmetics [19], and environment protects [20]. Among these applications, there are several papers demonstrated that CD's cavity can strongly interact with calcium to inhibit both the crystallization of calcium carbonate and attachment of scale on steel surface [15]. Polyethylene glycol (PEG) is an innoxious [21–23], neutral and nonionic surface active agent with the hydrophilic groups (–OH and –O–) and hydrophobic group (–CH_2–CH_2–) [24]. The effects of PEG on the nucleation and crystal growth of $CaCO_3$ have attracted scientists interested in scale inhibitor research [25,26]. However, single composition of β-CD or PEG used as a scale inhibitor barely achieves the desired anti-scaling effect. It was well demonstrated by many researchers that some co-inhibitors could effectively improve inhibition efficiency of organic scale inhibitor [27].

In the work, no phosphate and nitrogen free scale inhibitor β-cyclodextrin–polyethylene glycol (β-CD–PEG) was studied by the related factor experiments. The samples of inhibited scale mass were further characterized by scanning electron microscopy (SEM) and X-ray powder diffractometry (XRD) to investigate the crystal morphology of the scale. Moreover, the samples were measured by thermogravimetry–differential thermal analysis to further illustrate the scaling mechanism. In addition, compatibility tests were taken to study its application in the shale gas field.

2. Experimental

2.1. Materials

β-Cyclodextrin, polyethylene glycol (M.W. 400), thionyl chloride, sodium hydroxide and absolute ethyl alcohol were of analytical grade purchased from Kelong Chemical Reagent Factory (Chengdu, China). $CaCl_2$, $NaHCO_3$, KOH, HCl and EDTA were all of analytical purity. The flow back water was collected from one shale gas field in Shaanxi. All the solvent used was double distilled water.

2.2. Synthesis of the β-CD-PEG

The molecular structure of β-CD–PEG is shown in Fig. 1. The synthesis process of bridged cyclodextrin with polyethylene glycol was composed within two parts. Firstly, the chlorinated polyethylene glycol monomer was prepared. Secondly, the chlorinated polyethylene glycol interacts with cyclodextrins. The whole preparation method was shown in the reported procedure [28,14].

2.3. Static scale inhibition experiment

Scale inhibition efficiency was tested as described in Standard Test Method (GB/T 16632-2008) by EDTA titration [29]. It should be pointed out that in order to avoid the introduction of other impurities. So, deionized water was used in accordance with this standard. The principle was to add water samples with and without the scale inhibitor, then determine the concentration of calcium ion and calculate the inhibition rate. The inhibition scale efficiency η was calculated by Eq. (1).

$$\eta = \frac{\rho_1 - \rho_0}{\rho_2 - \rho_0} \times 100\% \quad (1)$$

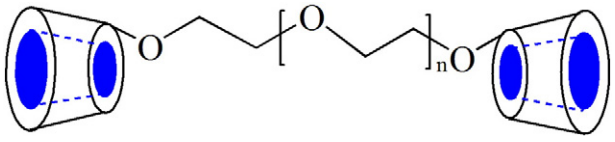

Fig. 1. Structural formula of β-cyclodextrin–polyethylene glycol.

where ρ_0 and ρ_1 were the Ca^{2+} concentrations without and with scale inhibitor, and ρ_2 was the initial Ca^{2+} concentration in the solution.

2.4. Characterization

Crystals of $CaCO_3$ in the presence and absence of β-CD–PEG exposed to 200 mg/L Ca^{2+} and 200 mg/L HCO_3^- solutions at 40 °C were collected after 6 h. The precipitate was filtered through a 0.45 μm pore size cellulose acetate filter paper and then characterized by SEM, XRD and TGA. The calcium carbonate scale samples were gold-coated and SEM images obtained using a Quanta450 environmental scanning electron microscope (FEZ Company, U.S.) at an accelerating voltage of 15 kV. Powder X-ray diffraction (XRD) patterns were recorded on an X Pert PRO MPD diffractometer (PANalytical B.V., Netherlands) with Cu Ka radiation. The phase identification was done by comparing the X-ray diffraction patterns of the crystals with the standard data available from the Joint Committee on Powder Diffraction Standards. Thermogravimetric analysis (TGA) was performed on a STA449F3 (Netzsch, Germany) instrument. The programmed heating range was from 40 °C to 800 °C at a heating rate of 5 °C/min under air atmosphere.

2.5. Compatibility test

First of all, the flow back water was added complex oxidizing agent and flocculating agent, successively. Then, the injection water was made after sedimentation and filtration. The composition of pretreated injection water determined as described by industry standards SY/T 0600-1997 is listed in Table 1. Though, there was no carbonate ion and sulfate ion, the 470 mg/L calcium ion and 984 mg/L bicarbonate ions can form $CaCO_3$ scale easily.

Mixed the treated flow back water and formation water in different volume ratio (0:5, 1:4, 1:1, 4:1 and 5:0) at 70 °C in a thermostat water bath for 72 h. Besides, the total volume is 100 mL for each sample. And, the turbidity was measured with WZS-180 turbidimeter (REX Instrument Factory, China).

3. Results and discussion

3.1. Analysis of the inhibition efficiencies for calcium carbonate scale

3.1.1. Effect of inhibitor dosage

The effects of the green antiscale agent β-CD–PEG for $CaCO_3$ scales were shown in Fig. 2. The tests were invested at different dosages of the novel polymer in the solution containing 200 mg/L Ca^{2+} and 200 mg/L HCO_3^- at 40 °C. In Fig. 2, the efficiency of scale inhibition increased obviously with the increasing inhibitor concentration before the concentration was 180 mg/L. When its dosage was over 180 mg/L, the more the added polymer, the slightly higher the efficiency of scale inhibition. Therefore, the dosage of 180 mg/L for the polymer was optimum, and the efficiency of scale inhibition reached 89.1%.

The β-CD–PEG that contains cyclodextrin cavity, hydroxyl group and ether bond can interact with Ca^{2+}. With the increase of inhibitors, the more Ca^{2+} ions were chelated. The inhibited efficiency was increased as well. When the concentration of the inhibitor was above the optimal value, the Ca^{2+} ions were almost chelated. The inhibition efficiency remained constant and not decreased as Xiaoxian Gu et al. described, due to the existence of PEG segment playing dispersive function [15].

3.1.2. Effect of bath time

The variation of the scale efficiency with bath time in the solution that contains 200 mg/L Ca^{2+}, 200 mg/L HCO_3^- and 180 mg/L inhibitor at 40 °C is shown in Fig. 3. Obviously, Fig. 3 shows that the highest efficiency was obtained at 6 h, because the inhibitor had sufficiently interacted with Ca^{2+} ions in the static system [30]. In addition, the scale inhibition dropped 7.0% with the increasing time from 6 h to 30 h. This might be caused by the destabilization of the scale inhibitor