Preparation and Performance Research of Anti-corrosion and Scale Inhibition Micro-Element Integrated Copolymer

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Abstract: China is rich in hydrothermal geothermal resources and has great development potential. More and more geothermal facilities have been put into production. Due to the presence of corrosive components such as oxygen, carbon dioxide, hydrogen sulfide, and chloride ions in geothermal water, uniform corrosion and scaling have occurred during the service of geothermal facilities. In response to the problem in China that the long-term scale inhibition effect of geothermal pipeline scale inhibitors and the common addition method of scale inhibitors in the middle and end sections is poor and scaling is still serious, microcapsules coated with melamine formaldehyde resin for anti-corrosion and scale inhibition have been developed. It can be slowly released in the pipeline and continue to act. The scale inhibitor PESA and preservative ODA were encapsulated into melamine formaldehyde (MF) wall materials by in-situ polymerization, and the MF/PESA-ODA copolymer was synthesized. The copolymer was characterized by Fourier transform infrared spectroscopy to investigate the relationship between the addition amount of the copolymer and the encapsulation rate. The anti-corrosion and scale inhibition performance of the microcapsules was tested by static and dynamic experiments. The results show that the synthesized microcapsules have a smooth and regular surface, uniform size, good stability, and an encapsulation rate as high as 92%. In the sustained-release experiment, the static release rate was as high as 80%, and the dynamic release rate was as high as 86.2%, indicating that the sustained-release performance of this microcapsule is excellent. It can achieve long-term scale inhibition in long-distance pipelines, protecting the pipelines while improving the utilization rate of anti-corrosion and scale

inhibition agents.

0 Introduction

Hydrothermal geothermal resources are abundant and have great development potential, and more and more geothermal facilities are put into production. Geothermal resource extraction is an integral part of oil production, and the effluent geothermal water often contains a complex composition of dissolved mineral ions (e.g., sodium, calcium, magnesium, carbonates, and sulfates), free oleohydrocarbons, suspended solids, and organic chemicals [1-4]. Geothermal facilities are affected by changes in pressure, temperature, and other conditions, and their corrosion and scaling tendency intensifies under the influence of geothermal water [5-13]. The intensifying tendency to scale will eventually lead to a large amount of scale formation and blockage of pipelines, which will bring great safety hazards and economic losses to the safe operation and maintenance of geothermal service equipment [14-18]。 In view of the problem that the long-term scale inhibition effect of the ordinary dosing method of geothermal pipelines in our country is poor in the middle and end of the period, and the scaling is still serious, a micro-element copolymer coated with melamine formaldehyde resin coated with anti-corrosion and scale inhibitor has been developed, which can be slowly released in the pipeline and continue to act, protecting the pipeline while effectively improving the utilization rate of the anti-corrosion and scale inhibitor.

1 Experimental part

1.1 Reagents and instruments

Melamine, formaldehyde, itaconic acid, 2-acrylamide-2-methylpropanesulfonic acid, hydroxyethyl methacrylate, citric acid, triethanolamine, emulsifier (OP-10), boric acid, EDTA,

anhydrous CaCl2, KOH, NaHCO3, Na2SO4. DF-101S Collective Heat Constant Temperature Heating Magnetic Agitator; YLE-1000 electric heating constant water bath pot; electric heating constant temperature drying oven; Thermo Fisher Scientific Nicolet iS20 Fourier Transform Infrared Spectrometer; ZEISS GeminiSEM 360 from Germany.

1.2.1 Preparation of melamine formaldehyde resin prepolymer

Weigh the melamine and formaldehyde solution in a ratio of 1∶3, mix and stir in a three-mouth flask, add an appropriate amount of triethanolamine to adjust the pH of the system to 8~9, stir the melamine formaldehyde mixture solution at a speed of 300 r·min-1 under the heating condition of 70 °C water bath, and after 10 minutes, the system becomes transparent, add distilled water of the same quality as the formaldehyde solution, continue to react for 50 minutes to obtain melamine formaldehyde resin prepolymer, cool to room temperature for later use.

1.2.2 Preparation of capsule core emulsion

Weigh 1g of PESA-ODA solution and put it in a three-mouth flask, add a certain amount of OP-10 emulsifier and deionized water to adjust the temperature of the water bath to 60°C, set the stirring rate of 700 $r\cdot^{min\text{-}1}$, and stir at high speed for 1 h to obtain a uniform white emulsion. The same method was used to prepare the core emulsion of 0.5 g and 1.5 g copolymers.

1.2.3 Preparation of copolymers

The cooled melamine formaldehyde resin prepolymer was added drop by drop to the core emulsion with a separating funnel, and the stirring rate was controlled at 500 r·min-1 at a water bath temperature of 60°C。 After the prepolymer drops are added, start to add citric acid solution, adjust the pH of the mixture to 3~4 to stop adding acid, keep the reaction for 3 h, the

reaction product is washed, filtered, and vacuum dried for 24 hours to obtain the required micropolymer powder, and add 0.5, 1 and 1.5 g of micropolymers as MF/PESA-ODA (0.5), MF/PESA-ODA (1), and MF/PESA-ODA (1.5).

1.3 Characterization analysis

The functional groups and chemical compositions of the copolymers and synthesized micropolymers in the wavenumber range of 4 000~500 cm-1 were identified by Thermo Fisher Scientific Nicolet iS20 Fourier Transform Infrared Spectrometer.

1.4 Calculation of encapsulation efficiency

0.2 g of microcopolymer was dispersed in 10 mL aqua regia for 24 h [16-17]. After completion, the above mixture was centrifuged and the supernatant was diluted with water to the appropriate concentration for UV-Vis absorption determination. The concentration of the copolymer is determined by a visible spectrophotometer based on a calibration curve obtained by measuring the absorbance of a series of concentrations of the solution at its specific wavelength. The encapsulation efficiency of the microelement copolymer is calculated according to Equation (1) e:

$$f = \frac{cMRV}{m} \times 100\%, e = \frac{fm_t}{m_i} \times 100\% \qquad (1)$$

Where:

f—core fraction of microelement copolymer;

e—the encapsulation efficiency of microelement copolymers;

c—molar concentration of copolymer determined by UV-Vis spectrophotometer;

M—molar mass of the copolymer;

R-dilution ratio;

V - volume of aqua regia;

m, m_t and m_i—the mass of the microcopolymers dispersed in aqua regia, the mass of the obtained microcopolymers and the mass of the copolymers added during synthesis.

1.5 Static scale inhibition experiment

Experimental procedure:

a. Use 20# steel, 10mm × 10mm × 2mm specimens; The specimen was polished with metallographic sandpaper and weighed as (m_0,g);

b. Simulate oilfield produced water according to the measured component configuration;

c. Put the corrosion specimen into the constant temperature oven for static periodic test;

d. Pour simulated water into the reactor to submerge the hanging sheet, turn off the reactor, set the temperature, and conduct a static period test.

f. Scanning electron microscopy test on the corrosion pendant after the experiment to observe its morphology. Keep the rest of the conditions unchanged, add microelement copolymer, place it in the same cycle and take it out, and perform scanning electron microscopy test to observe its morphology

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2 Results and discussion

2.1 Functional groups and composition analysis

In recent years, Fourier transform infrared spectroscopy has been widely used and is often used as a key technology for monitoring the composition of functional groups in organic/inorganic structures. Based on infrared spectroscopy technology, the infrared absorption peak of the sample was analyzed, and its functional group composition and blending were explored

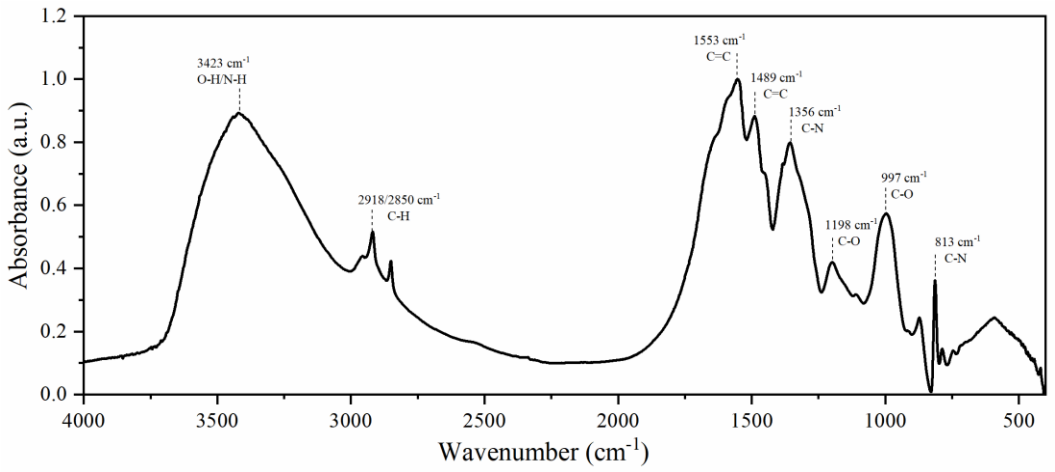


Fig.1 Infrared spectral characteristics of octadeamine, melamine formaldehyde resin, and polyepoxysuccinic acid polymerization samples

The infrared characteristics of the samples of octadecylamine, melamine formaldehyde resin, and polyepoxy succinic acid polymerization are shown in Figure 1 above. The main characteristics of the sample are relatively close to those of melamine-formaldehyde resin. For example, the absorption peak of the sample at 3423 cm^{-1} belongs to the O-H and N-H stretching vibration modes. The absorption peaks at 1546 cm^{-1} and 1489 cm^{-1} are related to structures such as C=C and C-N in melamine-formaldehyde resin; The absorption peak at 1356 cm^{-1} belongs to the bending vibration mode of C-N and methylene. At 813 cm^{-1} is the out-of-plane bending vibration absorption peak of the triazine ring in melamine formaldehyde resin, which is an important feature of melamine formaldehyde resin. In addition to the absorption peak of melamine-formaldehyde resin, the significant stretching of the absorption peak at 3423 cm^{-1} in the sample indicates the presence of a complex hydrogen bond interaction network among polymer molecules, which is an important feature of the extensive introduction of polar groups such as N-H. In addition, the appearance of sharp peak shapes at 2918 cm^{-1} and 2850 cm^{-1} also indicates the successful binding of the C-H structure of the octadecylamine long-chain alkane. The stretching of the absorption peak at 1553 cm^{-1} and the strong C-O absorption peak at 997 cm^{-1} are mainly related to the doping of the polyepoxysuccinic acid structure. The appearance of the above absorption peaks indicates the successful polymerization of octadecylamine, melamine formaldehyde resin and polyepoxysuccinic acid.

2.2 Sealing rate

In the three types of microcapsules, MF/PESA-ODA (0.5), MF/PESA-ODA (1), and MF/PESA-ODA (1.5), with the increase of the core material, the microcapsules will agglomerate, causing the copolymer scale inhibitor to be trapped between the microcapsules instead of being encapsulated inside the microcapsules. The encapsulation rate of the three microcapsules was above 72%, and the encapsulation rate of MF/PESA-ODA (0.5) was high at 81%, but with the increase of copolymers, the encapsulation rate gradually decreased, and the encapsulation rate of MF/PESA-ODA (1) and MF/PESA-ODA (1.5) was 78% and 72%, respectively. Therefore, excessive addition will cause agglomeration to deteriorate, and the capsule wall formed by the synthesized microcapsule product is more likely to rupture, and the coverage rate will also be reduced.

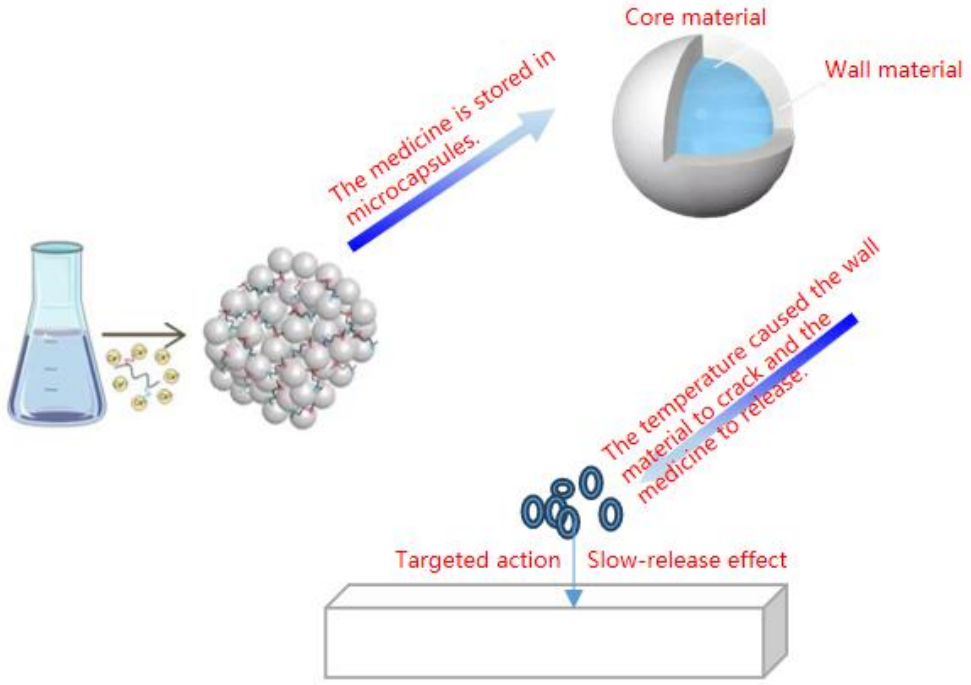


Fig. 2 The mechanism of microcapsule sustained-release effect

2.3 Static scale inhibition experiment

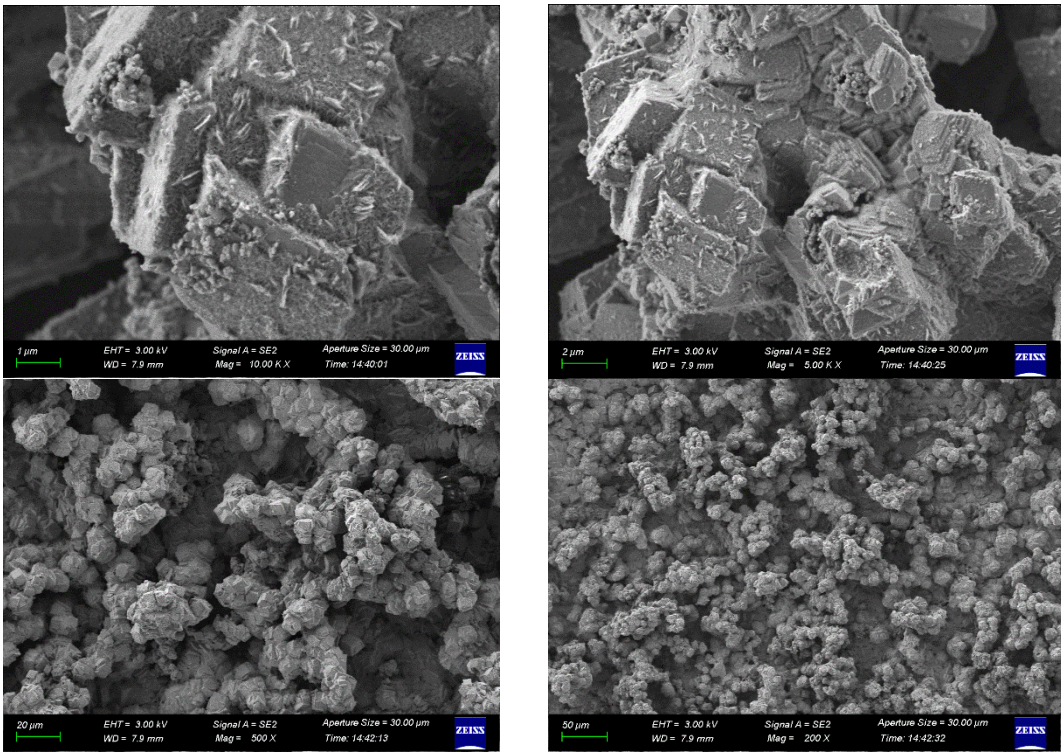


Fig. 3 SEM diagram of corrosion pendants after addition of micropolymers

The corrosion-scale mechanism and the action mechanism of corrosion inhibitors and scale inhibitors in different cycles were evaluated by static method, and the morphology was analyzed by scanning electron microscopy (SEM) in different experimental environments. The corrosion hanging sheet without scale inhibitor presents a regular strip structure, with a smooth surface and dense structure. The surface shape after the addition of micropolymer becomes irregular, and the surface is jagged, which inhibits the process of crystal growth, resulting in the crystal cannot grow in an orderly manner, and the crystal lattice is distorted, thus destroying its growth habit.

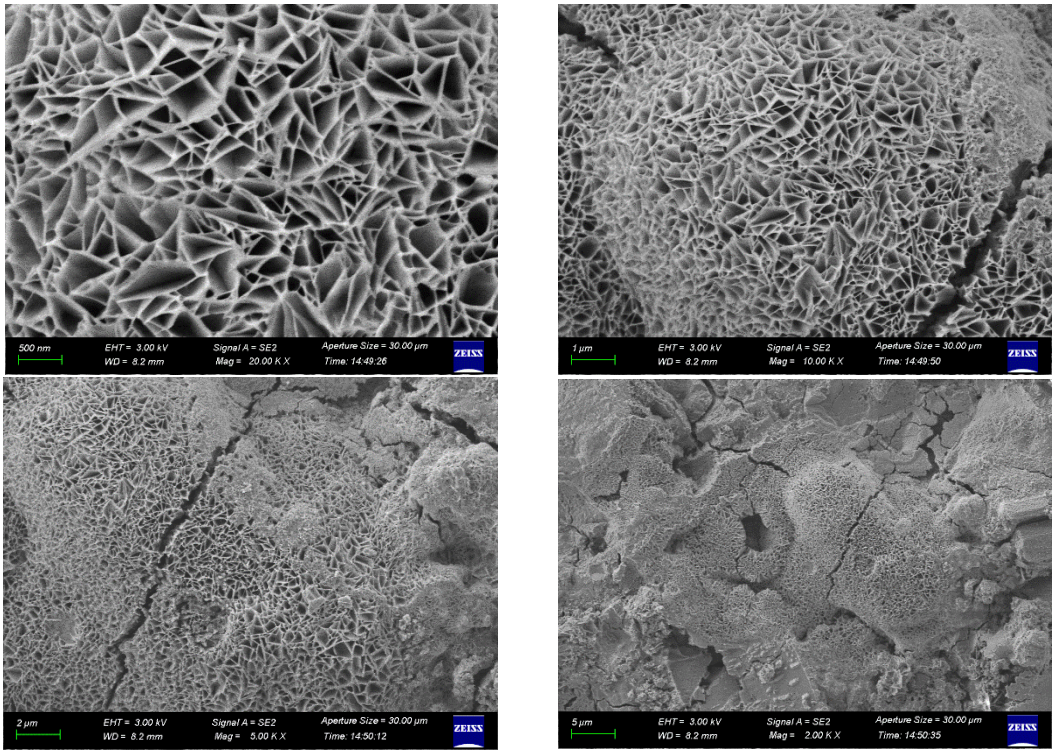


Fig. 4 SEM image of corroded pendants without the addition of micropolymers

3 Conclusion

Melamine formaldehyde micropolymer was synthesized by in-situ polymerization using melamine-formaldehyde resin as wall material and copolymer scale inhibitor as core material, and the encapsulation rate of the synthesized micropolymer was up to 81%. Under the premise of not affecting the effect of scale inhibitors, it can have a strong chelation, dispersion and lattice distortion effect on Ca2+, inhibit crystallization and scale, achieve the purpose of long-term continuous scale inhibition, improve the utilization rate of scale inhibitors, avoid a large amount of waste of scale inhibitors, and can effectively protect oil and gas exploitation equipment.

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