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Synthesis and properties of a MEAS quadripolymer scale inhibitor

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ABSTRACT

A novel quadripolymer scale inhibitor was prepared from maleic anhydride (MA), epoxy succinic acid sodium (ESAS), acrylamide (AM) and sodium allyl sulphonate (SAS), and the polymerisation was initiated by persulphate ammonium. This study determined the optimal synthesis conditions for the scale inhibitor by the orthogonal test, and investigated scale inhibitor dosage, systematic pH values and temperature on the scale inhibitor anti-scaling properties. The results showed that the optimal conditions of synthesis were as follows: the mass ratio of persulphate ammonium to total monomer was 15%, the monomer molar ratio for n(MA):n(ESAS):n(AM):(SAS) was 1:1:0.6:1, the reaction temperature was 90℃ and the reaction time was 3 h. When the temperature was 50℃, the pH value was 10, the scale inhibitor dosage was 20 mg/L and the calcium carbonate anti-scaling rate was 96%. The infrared spectra indicated that the synthetic copolymer contained the target functional groups. Scanning electron micrographs showed that the quadripolymer scale inhibitor mainly played roles in complexation and solubilisation. The practical application of the inhibitor led to an improved anti-scaling effect.

Keywords: Copolymer; Orthogonal test; Scale inhibitors; Calcium carbonate

1. Introduction

In recent years, the use of water-soluble polymers in water treatment systems has become more extensive. Polymer types of scale inhibitors are mainly divided into natural polymers and synthetic polymers. Due to unstable performance, complex components and the large quantity necessary for application, natural polymers are rarely used now. Synthetic polymer scale inhibitors overcome the shortcomings of natural polymer scale inhibitors; with their wide variety, flexible synthetic methods, high anti-scaling rate, good stability, easy control of molecular weight, broadly applicable water quality range and many other advantages, they have developed rapidly [1–3]. Research and development of polymer scale inhibitors is a hot topic in water treatment chemicals. Polymer scale inhibitors with high molecular weight are one of the most active areas of current scale inhibitor studies [4–6]. At present, polymer scale inhibitors include the carboxylic acid class, containing phosphorus-like, sulphonic acid class and green environmental protection class polymers. Carboxylic acid types of polymers, including acrylic acid, maleic acid and anhydride copolymers, have a strong chelating ability for Ca^{2+}, Mg^{2+}, Ba^{2+}, Fe^{3+}, Cu^{2+} and other metal ions [7]. Phosphorus class polymers are formed by

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copolymerisation of hypophosphorous acid and other monomers [8]. Sulphonic acid type polymers are mainly synthesised by sulphonic acid monomer copolymerisation and the formation of a scale inhibitor [9]. They have good anti-scale dispersion effects. The polyepoxysuccinate class of polyaspartic green-based polymers have good biological degradability [10]. Homopolymers have only one structural unit; so, they have only one application relating to a low anti-scaling rate. Copolymers have two structural units, including chelating groups and sorptive groups; so, they have multiple functions, such as solubilisation, dispersion, condensation, electrostatic exclusion and collaboration, leading to a higher anti-scaling rate [11–13]. Recently, the most commonly used scale inhibitor has been a copolymer of acrylic acid and maleic acid as the main body. At the same time, the introduction of amide, hydroxyl, sulphonic, etc. variety of functional groups in the molecule improves the stability of scale inhibition, as well as the scale inhibitor performance [14,15].

In this study, with maleic anhydride (MA), epoxy succinic acid sodium hydrogen (ESAS), acrylamide (AM) and sodium allyl sulphonate (SAS) as the monomers, and ammonium persulphate as the initiator, a new non-toxic and non-phosphorus quadripolymer was synthesised. The study determined the optimal synthesis conditions for the scale inhibitor by the orthogonal test and evaluated its performance. The synthetic quadripolymer had a better anti-scaling effect on calcium carbonate.

2. Materials and methods

2.1. Reagents and instruments

MA, AM, SAS, ethylene diamine tetraacetic acid disodium (EDTA), magnesium chloride ($MgCl_2·6H_2O$), anhydrous calcium chloride, sodium hydroxide, sodium bicarbonate, sodium carbonate, sodium chloride, anhydrous sodium sulphate and calcium carboxylic acids were of analytical grade, and were purchased from Harbin Chemical Reagent Factory. Epoxy succinic acid hydrogen sodium (ESAS) is our own product.

The instruments used are as follows: Type 202 constant-temperature drying oven and KDM-type electric heating temperature controlled sets (the Shanghai Shenghua Instrument Co., Ltd), HH-S26s digital display constant temperature water bath pot and DJ1C increase force of an electric stirrer (the Jintan Dadi Automation Instrument Plant), BS-210S electronic balance (Sartorius, Germany), MB154S Fourier transform infrared spectrometer (Bomem, Canada) and LEO-1530VP scanning electron microscope (SEM) (Leo, Germany).

2.2. The synthesis of the quadripolymer scale inhibitor

First, a certain amount of ESAS and AM was added to the flasks with a mechanical stirrer, reflux condenser, dropping funnel and thermometer, while continuously stirring. Second, MA and distilled water were added in equal proportions, and the pH value of the solution was adjusted to 4∼5 with sodium hydroxide (7 mol/L). Third, SAS was added. When the temperature reached 80℃, the temperature was controlled and ammonium persulphate was added drop by drop. Then, the temperature was raised to 90℃ and the reaction took place at this temperature. The product obtained was the copolymer. The coarse product was allowed to dry by evaporation, then solubilised in methanol and the methanol solution was put into ethanol. The resulting precipitate was washed several times, and the reaction solution was diluted and passed through a strongly acidic ion-exchange column before the solution was evaporated under vacuum, yielding the solid copolymer.

2.3. Performance evaluation of the scale inhibitor

2.3.1. Determination of the water solubility of the scale inhibitor

The mass concentration of the quaternary copolymer solution was prepared to 1% and placed on a magnetic stirrer with a rotation speed of 300 r/min for 5 min. The temperature of the water bath was maintained at 25℃ by heating for 10 min. Inhibitors were then removed and observed under natural light.

2.3.2. Determination of the solid content of scale inhibitor

The sample was mixed uniformly, placed in a constant temperature drying oven and dried at 120℃ for 8 h; then, it was moved into the dryer, cooled for 30 min to room temperature and the mass fraction of the solid content was calculated.

To calculate the mass fraction of the solid content, Eq. (1) was used:

$$\omega = (m_3 - m_1)/(m_2 - m_1) \tag{1}$$

where ω is the solid content mass fraction of the sample, m_1 is the mass of the dry beaker, m_2 is the mass of the sample and beaker before being dried and m_3 is the mass of the sample and beaker after being dried.

2.3.3. Determination of the calcium carbonate anti-scaling rate of the scale inhibitor

The anti-scaling rate measurement used the EDTA titration method. The specific method was as follows: the quadripolymer scale inhibitor was added to prepared water samples containing a certain amount of calcium and bicarbonate ions, heated to a constant temperature in a water bath for a certain period of time, then cooled to room temperature and filtered. The filtrate was titrated with a standard solution of EDTA.

To calculate the anti-scaling rate of the scale inhibitor, Eq. (2) was used:

$$E_f = (V_1 - V_0)/(V - V_0) \tag{2}$$

where E_f is the anti-scaling rate of the scale inhibitor, V_1 is the consumptive EDTA volume of the sample in the presence of the inhibitor, V_0 is the consumptive EDTA volume of the sample in the absence of the inhibitor and V is the consumptive EDTA volume of the sample with certain calcium ions.

2.4. Representation of the structure and molecular weight of the copolymer

A small amount of dried and trace quadripolymer scale inhibitor was ground with quantitative KBr prepared in advance and was made into a thin chip. A MB154S Fourier infrared spectrometer was used for synthetic copolymer structure determination. The viscosity method was used to determine the relative molecular weight of the polymer products [16].

2.5. Mechanism of the scale inhibitor

An LEO1530 SEM was used to analyse the scale sample (after treatment with the quadripolymer scale inhibitor or without) and the anti-scaling mechanism was investigated, based on SEM. By observing the scale sample morphology, crystalline state, crystal scale and the number of particle size changes, the anti-scaling effect of the copolymer inhibitor on calcium carbonate scale formation was analysed.

2.6. Evaluation of the copolymer scale inhibitor

The copolymer scale inhibitor was added in the field, and the anti-scaling rate was tested using the coupon method. A hanging piece was placed in the pipeline for 80 days and removed for weighing after drying at 100℃, in order to measure the amount of scaling. The anti-scaling rate was determined by comparing the amount of the scale on hanging pieces from the blank pipe and the test pipe segment.

3. Results and discussion

3.1. Determination of the optimised synthesis conditions

Four factors, including the amount of the initiator, monomer ratio, polymerisation temperature and polymerisation time, were investigated with regard to the performance of the calcium carbonate scale inhibitor; three levels were assessed for each factor. The test indicator was the anti-scaling ability of the quadripolymer scale inhibitor on calcium carbonate scaling and the experiment was done using the $L_9(3^4)$ orthogonal table. The designed factor-level table is shown in Table 1. The designed orthogonal test programme and results are shown in Table 2.

Table 2 shows the impact of various factors on the synthetic products of calcium carbonate scale performance in the order A, B, C and D, which refer to the polymerisation temperature, polymerisation time, amount of initiator and monomer ratio. The optimal synthetic condition was $A_3B_1C_3D_2$, namely polymerisation temperature of 90℃, polymerisation time of 3 h, initiator dosage of 15% of the total monomer weight and a monomer molar ratio of n(MA):n(ESAS):n(AM):(SAS) set to 1:1:0.6:1. The verification test was performed under these conditions; the anti-scaling rates of calcium carbonate scale were 92.15, 92.26 and 92.10% and the average anti-scaling rate was 92.17%.

Table 1
The synthesis influence factors and levels of quadripolymer

Levels	A: Polymerisation temperature (℃)	B: Polymerisation time (h)	C: The amount of initiator (%)	D: n(MA):n(ESAS):n(AM):n(SAS)
1	70	3	5	1:1:0.6:0.8
2	80	3.5	10	1:1:0.6:1
3	90	4	15	1:1:0.6:1.2

Table 2
The programs and results of the orthogonal test

Test number		A	B	C	D	The anti-scaling rate (%)
1		1	1	3	1	78.12
2		1	2	2	2	62.13
3		1	3	1	3	40.20
4		2	2	3	3	71.23
5		2	3	2	1	67.09
6		2	1	1	2	78.49
7		3	3	3	2	84.82
8		3	1	2	3	78.30
9		3	2	1	1	78.38
The average anti-scaling rate (%)	K_1	60.15	78.30	65.69	74.53	
	K_2	72.27	70.58	69.17	75.15	
	K_3	80.50	64.04	78.07	63.24	
Ranges		20.35	14.26	12.38	11.91	

3.2. Performance evaluation of the quadripolymer scale inhibitor

3.2.1. Determination of the water solubility and solid content (mass fraction) of the quadripolymer scale inhibitor

The scale inhibitor liquid was clear and transparent in the beaker, when observed under natural light. There were no floating materials on the liquid surface and no deposited materials on the bottom of the beaker. Therefore, the sample was determined to be dissolved. The result of the determination showed that the solid content calculated by the mass fraction of this scale inhibitor was 58.26%.

3.2.2. Infrared analysis of the quadripolymer scale inhibitor

Analysis of the structure of the synthetic anti-scaling agent used infrared spectroscopy. The FTIR spectra of the quadripolymer are shown in Fig. 1. The characteristic absorption wave numbers were 3456.22, 1669.88, 1400.83, 1197.89 and 1126.04 cm^{-1}, in the FTIR spectra. The strong characteristic absorption peak at 1669.88 cm^{-1} was the stretching vibration of the C=C bond in olefin and the C=O bond in amide, indicating that the copolymer contained AM. Because the characteristic absorption peak of MA, caused by symmetrical and asymmetrical stretching vibrations of the C=O bond at 1,780 cm^{-1}, did not appear, and no vibration absorption peak of the C=C bond of MA was found near 1,645 cm^{-1}, the MA was considered to have been completely hydrolysed. The absorption peak of the stretching vibration that appeared at 1400.83 cm^{-1} was the C=O bond in COO^{-}. The stretching vibration peak of methylene C–H in CH–O–C (a ter closed-loop) did not appear at 3,031 cm^{-1}, suggesting that the open-loop ESAS was involved in the reaction. The characteristic absorption peak of allyl sulphonic acid appeared at 1126.04 and 1197.89 cm^{-1}. The figure also showed that the absorption peak of the CH_2=in CH_2=CH– (905 cm^{-1}) and =CH– (985 cm^{-1}) could not be found; so, the synthetic product was the quaternary copolymer. The formula of the quaternary copolymer was:

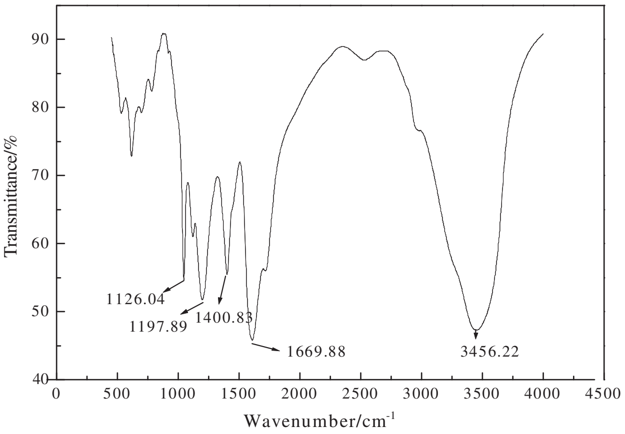


Fig. 1. FTIR spectra of the quadripolymer.

Using the viscosity method for the determination of molecular weight of the quaternary copolymer gave a value of 1.32 × 10^5.

$$-\left[H_2C-\underset{O=CNH_2}{HC}\right]_x\left[\underset{CCOOCOOH}{HC-CH}\right]_y\left[O-\underset{COOH}{CH}-\underset{COOH}{CH}\right]_z\left[CH_2-\underset{CH_2\,SO_3Na}{CH}\right]_w-$$

3.3. The effects of the quadripolymer scale inhibitor on the calcium carbonate anti-scaling rate

3.3.1. The effects of quadripolymer scale inhibitor dosage on the calcium carbonate anti-scaling rate

The roles of a scale inhibitor in solution are chelation, dispersion and lattice distortion, in order to prevent scale formation and deposition. Normally, a scale inhibitor has an optimal concentration. When the concentration is lower or higher than this, the effect will be reduced; this strange effect is called the "dissolve limit effect" of the scale inhibitor. When the temperature was 70℃, pH was 12 and other conditions were fixed, the anti-scaling rate with different concentrations of the quadripolymer was determined by applying the method of calcium carbonate anti-scaling rate determination; the results are shown in Fig. 2. It could be seen that the quadripolymer calcium carbonate anti-scaling rate first increased and later decreased when the scale inhibitor concentration was between 10 and 30 mg/L in a small scope, with the increase in the amount of scale inhibitor, which was caused by the scale inhibitor's low-dose effect. Polyphosphates, organic phosphates and polycarboxylic acid scale inhibitors all have such an effect [17].

3.3.2. The effect of the pH of the system on the calcium carbonate anti-scaling rate

When the scale inhibitor dosage was 20 mg/L, temperature was 70℃ and other conditions and measuring methods were applied as in the above system, the system pH values ranging from 7 to 12 affected the calcium carbonate anti-scaling rate of the quadripolymer scale inhibitor. The results are shown in Fig. 3. From Fig. 3, it can be seen that when the pH value increased, the anti-scaling rate of the quadripolymer first increased and later decreased. When the pH value was 10, the quadripolymer anti-scaling rate achieved the maximum rate. When the pH value was greater than 10, with the increase in pH, the calcium ion concentration decreased. This was due to the fact that the saturation solubility of calcium ions increased with an increase in pH value. However, when the pH value was higher, carboxylic acid anions, playing the anti-scaling role in the scale inhibitor, were neutralised; so, the calcium and magnesium ion precipitation trend enhanced the solution and the anti-scaling rate descended. The conclusion could be made that the carboxylic acid anion has a great contribution to anti-scaling.

3.3.3. The effect of temperature on the calcium carbonate anti-scaling rate

When the dosage of the scale inhibitor was 20 mg/L, pH value was 10, and other conditions and measuring methods were applied as for the above system, the measuring temperature ranging from 50 to 90℃ had an effect on the quadripolymer scale inhibitor calcium carbonate anti-scaling rate. The results are shown in Fig. 4. From this figure, it can be seen that when the temperature increased, the anti-scaling rate of the quadripolymer decreased somewhat. The quadripolymer anti-scaling rate of calcium carbonate decreased with increasing temperature. When the temperature was in the range of 50–90℃, the anti-scaling rates were greater than 70%. However, when the temperature was increased to 80℃, the

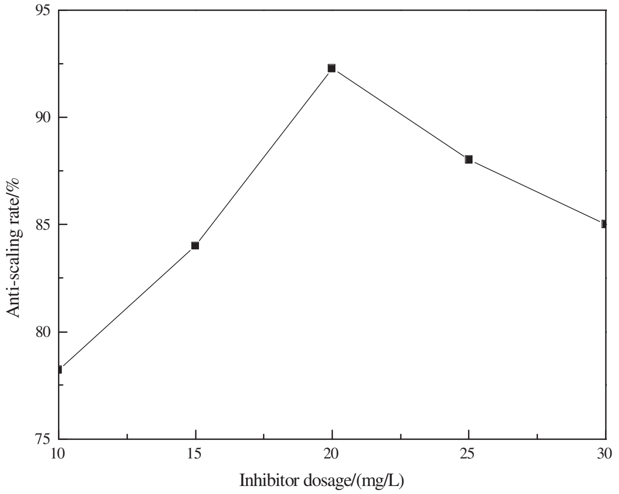


Fig. 2. The effect of scale inhibitor's dosage on calcium carbonate anti-scaling rate.

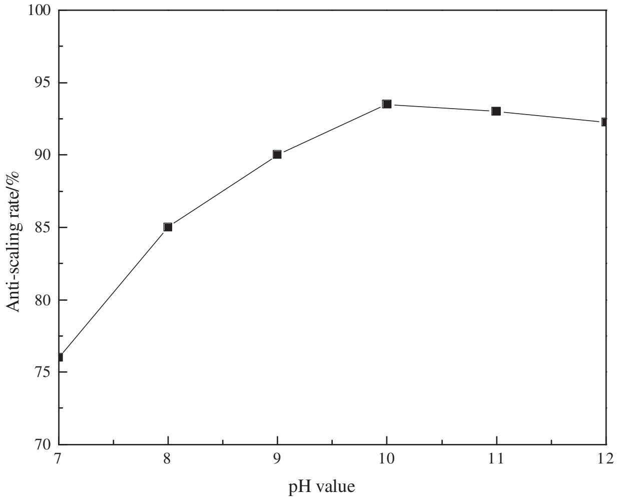


Fig. 3. The effect of pH value on calcium carbonate anti-scaling rate.

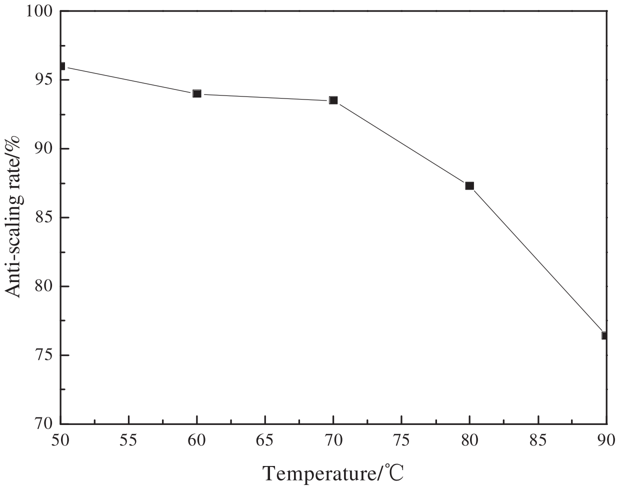


Fig. 4. The effect of temperature on calcium carbonate anti-scaling rate.

anti-scaling rate suddenly dropped significantly. This indicates that the anti-scaling rate of the quadripolymer is largely affected by temperature and its temperature resistance is poor. The influence of temperature mainly changed the solubility of the salts, which were easily scaled. The solubility of calcium carbonate decreased with an increase in temperature and gradually separated out and formed the scale.

3.4. *Anti-scaling mechanism of the polymer*

Scale inhibitor mechanisms are mainly lattice distortion, complex solubilisation, threshold effects and electrostatic repulsion [18–20]. The SEM of the calcium carbonate scale showed that by not adding the copolymer scale inhibitor, the scale morphology emerged as small particles and rod-like crystalline states, which were closely intertwined. The size of the particles was no more than 10 μm. The supersaturation of calcium ions caused crystal core and solid phase embryos and then generated particles. Interconnection between the particles created the scale, which is so dense and uniform that it is not easy to dissolve. In the presence of the copolymer scale inhibitors, the scale of the micro-scale layer was loose and the size of particles and rod-like crystalline structures was enlarged, while the amount of crystallisation decreased. All of these data show that the copolymer had a good anti-scaling effect on calcium carbonate scale.

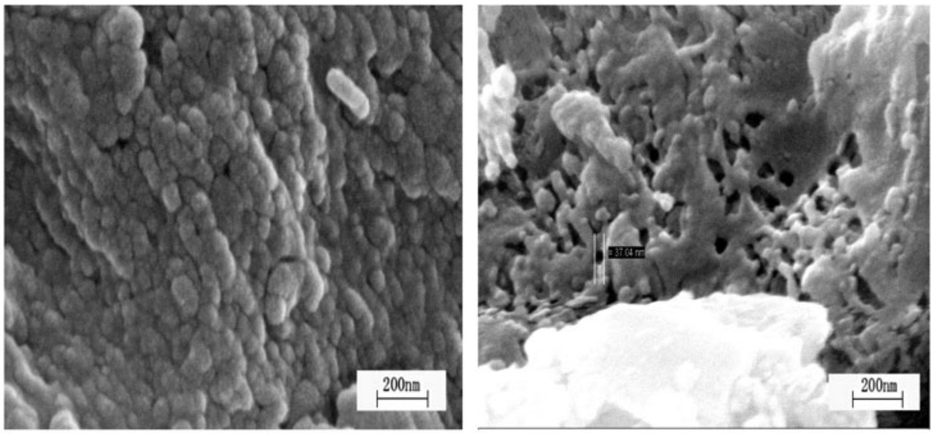
The anti-scaling role of the polymer was mainly determined by two aspects. The first is complexation. These anionic scale inhibitors in aqueous solution can be dissociated into anions, and sulphonic acid and carboxylic acid anions undergo stronger complexation with Ca^{2+} ions to form complexes which are soluble in water. The more the polymer present, within a certain range, the greater the level of complexation. The other aspect is solubilisation. The polymer molecules can adsorb calcium carbonate microcrystalline suspensions in water, which leads to calcium carbonate microcrystalline structures dispersed in water without precipitating out; this correspondingly increases the solubility of calcium carbonate in water and provides an anti-scaling effect (Fig. 5).

3.5. *The scene application evaluation of the scale inhibitor*

In contrast to practical scale inhibitors (A and B), which are purchased by oilfield chemical factories, the performance of the quadripolymer scale inhibitor had been designed for scene application evaluation. The results are shown in Table 3, showing that the quadripolymer scale inhibitor (MEAS) had a better effect in practical applications, as the anti-scaling rate was greater than 90% and could achieve the purpose of effective anti-scaling in pipelines. The South 2-16 was a seriously scaled oil transfer station. After dosing with the MEAS, the inspection proceeded prior to the dredging of the furnace. The scale inhibitor had a good anti-scaling effect on the pyrotechnics pipe. The South 2-12 oil transfer station did not use a scale inhibitor, and the furnace had to be overhauled due to a collapse and perforation on the fire tube. Its fireworks tube surface contained compacted hard scale and was accompanied by severe corrosion.

Table 3
The practical effect contrast among the scale inhibitors in South 2-16

Scale inhibitor	The scale sample weight (mg)	Average scale thickness (mm)	Scaling speed ($mg\,cm^{-2}\,d^{-1}$)	The anti-scaling rate (%)
MEAS	34.8	0.2	0.42	92.3
A	63.1	0.4	0.75	86.3
B	121.7	0.8	1.48	72.9
None	448.9	2.6	5.47	–



A. Not adding the scale inhibitor **B. Adding the scale inhibitor**

Fig. 5. SEM image of calcium carbonate scale adding and not adding quadripolymer.

4. Conclusions

In this paper, using the materials MA, epoxy succinic acid sodium hydrogen (ESAS), AM and SAS as monomers, a new, non-toxic, non-phosphorus quadripolymer (MEAS) calcium carbonate scale inhibitor was synthesised. The best conditions for synthesis were as follows: initiator dosage of 15% of the total mass of the monomer, monomer ratio of n(MA):n (ESAS):n(AM):n(SAS) set to 1:1:0.6:1, polymerisation temperature of 90°C and the polymerisation time of 3 h. Under the optimal synthetic conditions, the anti-scaling rate of the copolymer on calcium carbonate was greater than 90% and the anti-scaling effect was good.

The performance of the copolymer was influenced by the scale inhibitor concentration, pH value and temperature. The anti-scaling activity of the polymer was mainly the result of complexation and solubilisation, and the practical application generated a good anti-scaling effect.

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