

Preparation of a novel hyperbranched polymer and its scale inhibition performance

Wei Xi¹, Shu-sheng Zhou²

¹ Jingzhou University, Jingzhou 434020, Hubei, China

² Jingzhou Jiahua Technology Co., Ltd., Jingzhou 434000, Hubei, China

Received 19 June, 2024

Calcium scale is easily deposited on pipeline surfaces under the influence of pressure and temperature, which leads to a decrease in oil and gas production. To effectively prevent scale formation, a new hyperbranched polymer based on Michael addition and amidation reactions has been developed, which is phosphorus-free and a highly effective scale inhibitor. It consists of ethylenediamine (EDA), methyl acrylate (MA) and succinic anhydride (SA) as raw materials, and its scale inhibition performance and mechanism were studied. According to the experimental results, at the concentration of 400 mg/L, the inhibition rates of HPA-COOH for CaCO₃ and CaSO₄ scales were 97.3% and 91.2%, respectively, indicating good scale inhibition performance. The addition of scale inhibitor (HPA-COOH) led to a significant decrease in the Z-potential and transmittance, which contributed to the formation of small and stable calcium scales in the solution and increased the dispersing efficiency of the scale inhibitor. In addition, the growth of CaCO₃ scale crystals was inhibited by HPA-COOH which crystallizes in a large and unstable form and results in a change in the crystal form of CaCO₃ scale.

Keyword: Hyperbranched polymer; Scale inhibition; CaCO₃ scale crystal; Michael addition reaction; Zeta potential value

Отримання нового гіперразветвлененого полімеру і його здатність інгібувати утворення накипу. Wei Xi, Shu-sheng Zhou

Кальцієвий накип легко відкладається на поверхні трубопроводів під тиском та температурою, що призводить до зниження видобутку нафти та газу. Щоб ефективно запобігти утворенню накипу, на основі реакцій приєднання Міхаєля та амідування було отримано новий надрозгалужений полімер, що не містить фосфору і є високоефективним інгібітором накипу. У вихідних реагентах були використані етилендіамін (ЕДА), метилакрилат (МА) та бурштиновий ангідрид (СА). Було вивчено ефективність та механізм інгібування утворення накипу. Результати експериментів показують, що при концентрації 400 мг/л ступінь інгібування НРА-СООН відкладень CaCO₃ та CaSO₄ склала 97,3% і 91,2% відповідно, що вказує на добрі характеристики інгібування відкладень. Додавання інгібітору відкладень (НРА-СООН) призвело до значного зниження значення дзета-потенціалу та коефіцієнта пропускання, що сприяло утворенню невеликих та стабільних кальцієвих відкладень у розчині та зростанню диспергуючої ефективності інгібітора солевідкладень. Крім того, НРА-СООН інгібувало зростання кристалів накипу CaCO₃, утворюючи велику і нестабільну кристалічну форму і призводячи до зміни кристалічної форми накипу CaCO₃.

1. Introduction

Scale formation is usually defined as the deposition of inorganic salts (calcium carbonate and calcium sulfate) from aqueous solutions; it reduces oil and gas production from wells and

slows down the accumulation and transportation of crude oil during field operation [1-3]. Calcium carbonate and calcium sulfate are easily deposited on pipeline surfaces under high pressure and temperature. Scale will cause significant delay or loss of production due to

narrowing or plugging of wells and pipelines with scale [4]. In the oil and gas industry, the most common inorganic scales such as CaCO_3 and CaSO_4 result in severe damage of field equipments, especially for the industrial water cooling system and oil production systems [5-6]. The injection of seawater to maintain reservoir pressure is one of the main causes of sulfate deposition [7]. The dissolution of CaSO_4 is more difficult than CaCO_3 and often requires the addition of chelating agents such as ethylene diamine tetraacetic acid (EDTA), ethanolamine-N, N-diacetic acid (HEIDA), N-(hydroxyethyl) ethylenediamine triacetic acid (HEDTA) and diethylene triamine penta acetic acid (DTPA) [8–10]. In addition, the dissolution of CaSO_4 is greatly influenced by the pH values of the well fluids. Much attention has been paid to how to prevent scale formation. Therefore, the use of the efficient scale inhibitor is very important for the stable production and operation of oil and gas wells [11].

Hyperbranched polymers have low viscosity, high fluidity, a large number of end groups, and their empty network structure can provide abundant binding sites, which can greatly improve their chelation ability with metal ions, better disperse complex ions and precipitated particles [12]. A large number of studies have shown that hyperbranched polymer is an ideal water treatment agent that used in scale inhibition. Yan [13] successfully prepared the hyperbranched scale inhibitor using epoxidized succinic acid, itaconic acid and sodium methylpropenesulfonic acid as raw materials. When the dosage of the scale inhibitor is 24 mg/L, the rates of inhibition of CaCO_3 and CaSO_4 scales are as high as 96% and 99%, respectively. Jensen [14] synthesized a new class of hyperbranched polymeric scale inhibitors using hyper-branched polyethyleneimines, sodium vinyl phosphonate and sodium vinyl sulfonate as raw materials. They can prevent the deposition of calcium carbonate and barium sulfate in dynamic tube blocking tests. Wang [15] prepared hyperbranched polyether corrosion and scale inhibitor with carboxyl and phosphorus, which has higher efficiency than existing inhibitors used for industrial water treatment. Water-soluble molecules or these polymers contain functional groups such as phosphonate or sulfonate. Scale inhibitors containing phosphorus and sulfur elements have good scale inhibition performance, but do not contribute to environmental protection [16]. Due to tightening environmental regulations, scale inhibitors

without phosphorus and sulfur have become the subject of research and development in the industry.

In this paper, the hyperbranched polymeric scale inhibitor without phosphorus and sulfur elements was prepared by using ethylenediamine (EDA), methyl acrylate (MA) and succinic anhydride (SA) as raw materials, and its scale inhibition performance and mechanism were studied.

2. Experimental

2.1. Materials

Analytical grade ethylenediamine (EDA), methyl acrylate (MA), methyl alcohol, sodium hydroxide (NaOH) and succinic anhydride (SA), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Analytical grade acetone was supplied by the Nanjing Chemical Reagent Co., Ltd. Analytical grade calcium chloride (CaCl_2), sodium bicarbonate (NaHCO_3), sodium sulfate (Na_2SO_4) and sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) were obtained from Chevron Phillips Chemical (China) Co., Ltd. The common scale inhibitors such as sodium tripolyphosphate (STPP), polyaspartate (PASP) and polyepoxysuccinic acid (PESA) were supplied by Jingzhou Jiahua Technology Co., Ltd. As a high-performance scale inhibitor, phosphonate terminated hyperbranched polyamide-amines (PTHP) was obtained from Shandong Aike Water Treatment Technology Co., Ltd.

2.2. Synthesis and characterization of scale inhibitor

Synthesis and route of the hyperbranched polymeric scale inhibitor are shown in Fig. 1. To carry out the addition reaction, 10 g of ethylenediamine (EDA), and 50 g of methyl alcohol were first added into a three-mouth flask equipped with stirrer, pressure-equalizing dropping funnel and reflux condenser. Afterward, 10 g of methyl acrylate (MA) was added into the funnel, followed by being slowly dripped into the flask for 3 hours. Then the reaction system was refluxed with continued stirring for 24 hours at 35 °C. Finally, the reaction system was purified by vacuum distillation to remove excess methyl alcohol and methyl acrylate, and hyperbranched polyamide-amine (HPA) was prepared.

To carry out the amidation reaction, 5 g of succinic anhydride was added into the flask containing hyperbranched polyamide-amine,

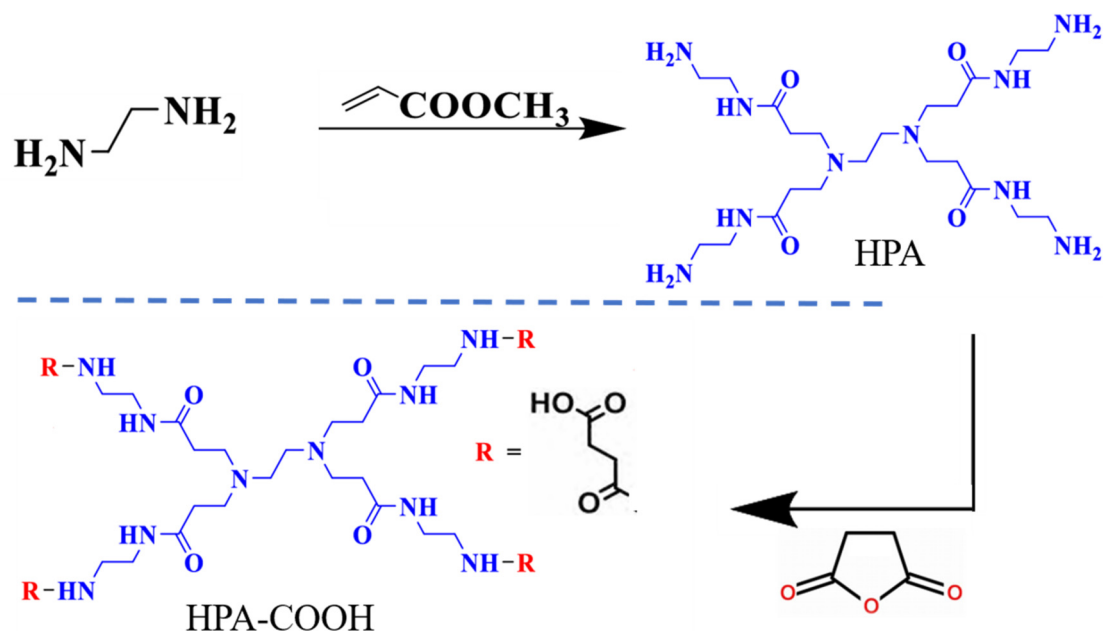


Fig.1 Synthesis and route of the hyperbranched polymeric scale inhibitor.

followed by maintaining the reaction temperature at 90 °C and stirring for 4 hours. Finally, the hyperbranched polymeric scale inhibitor (HPA-COOH) was obtained by washing with acetone and drying in an oven at 80°C.

The structure of the hyperbranched polymeric scale inhibitor (HPA-COOH) was characterized by a Nicolet710 Fourier transform infrared spectrometer.

2.3. Scale inhibition properties of HPA-COOH

According to the national standard of People's Republic of China (GB/T 16632-2008), experiments were conducted to inhibit the formation of static scale using calcium deposits as an example. Specifically, calcium chloride (CaCl_2), sodium bicarbonate (NaHCO_3), sodium sulfate (Na_2SO_4) and sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) were dissolved in 1000 mL deionized water. The solution D was used as a buffer solution. The amounts of added substances are shown in Table 1. 250 mL deionized water, 7.19 mL solution A, 20 mL solution D and 14.5 mL solution B were added into glass bottles with lid, followed by stirring evenly. Then, the mixtures were placed in an oven for a few hours at 80 °C, and CaCO_3 scale was obtained. In addition, according to the above experimental method, 7.19 mL solution C was used instead of 14.5 mL solution B to obtain CaSO_4 scale. The Ca^{2+} concentra-

Table 1 Formulations of the standard solutions

Solution	Sample	Dosage/ g
A	CaCl_2	16.7
B	NaHCO_3	25.2
C	Na_2SO_4	21.3
D	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	3.8

tion of the above mixtures with and without the hyperbranched polymeric scale inhibitor (HPA-COOH) was measured by titration with EDTA standard solution. Finally, the scale inhibition efficiency (η) of HPA-COOH was calculated according to eq. (1).

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

where η is the efficiency of the scale inhibitor; ρ_0 is the Ca^{2+} concentration in the mixture before holding; ρ_1 is the Ca^{2+} concentration in the mixture after holding; and ρ_2 is the Ca^{2+} concentration in the mixture with different concentrations of scale inhibitor after holding.

2.4. Dispersion properties of HPA-COOH

The dispersion properties of iron oxide are often used as an important basis for testing the ability of a scale inhibitor to disperse calcium scale in water [17]. In general, the dispersing ability of a scale inhibitor towards calcium de-

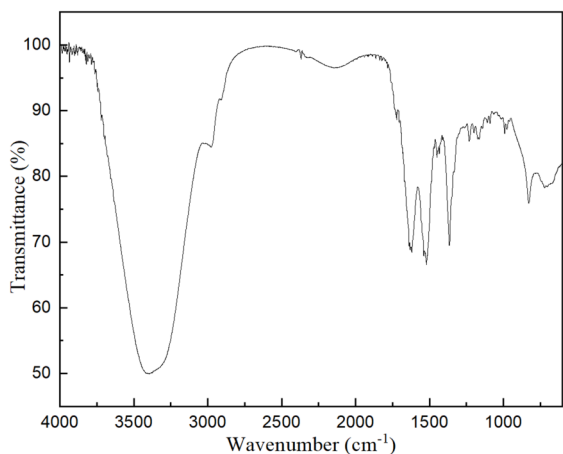


Fig. 2 FTIR spectrum of the hyperbranched polymeric scale inhibitor.

posits is measured by the transmittance and zeta potential of the solutions. Under the same conditions, the greater the absolute value of Zeta potential and the lower the transmittance, the smaller and more stable calcium scale formed in the solution, and the better dispersion capacity of the scale inhibitor [18].

The Fe^{2+} solution of 10 mg/L concentration was prepared by dissolving ferrous sulfate heptahydrate in deionized water, followed by adding the scale inhibitor and a calcium chloride solution, where the Ca^{2+} concentration was 150 mg/L. The pH value of the mixture was adjusted to 7 by sodium hydroxide and then adjusted to 9 by sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), followed by being placed in an oven for 8 hours at 80 °C. After cooling to room temperature, the transmittance of the mixture was measured by UV-500 spectrophotometer at the wavelength of 420 nm, and the zeta potential value of the mixture was measured by a Nano ZS Zeta potentiometer.

2.5. SEM analysis

The filtered CaCO_3 scale was washed several times with deionized water, dried and tested using a JSM7200F scanning electron microscope (SEM) to analyze the scale inhibition mechanism.

3. Results and Discussion

3.1. Infrared Spectrum of HPA-COOH

The FTIR spectrum of the hyperbranched polymeric scale inhibitor (HPA-COOH) is shown in Fig. 2. As indicated, the spectrum absorption peak at 3325.6 cm^{-1} was the stretching vibration of the hydroxyl group. The peak at 1730.5 cm^{-1} belongs to the stretching

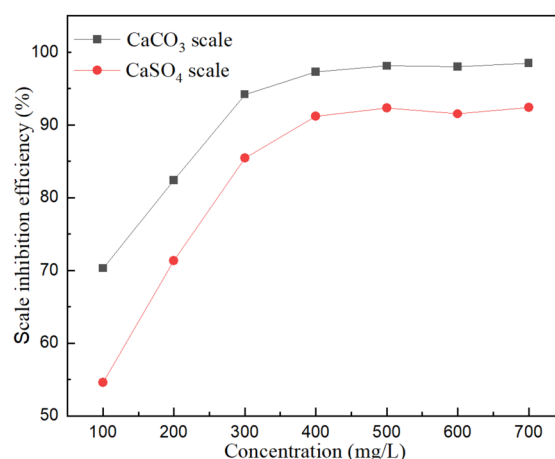


Fig. 3 Effect of HPA-COOH concentration on scale inhibition.

vibration of the carbonyl group in the carboxyl group, which indicated the appearance of carboxyl groups in the synthetic product. The peak at 2926.0 cm^{-1} was the characteristic band of $-\text{CH}_2$. The absorption peaks at 1650.6 and 155.8 cm^{-1} correspond to the stretching vibrations of $-\text{C}=\text{O}$ and N-H respectively, indicating the occurrence of an amidation reaction in the synthesis. The peaks at 1330.7 , 1125.0 , and 1034.2 cm^{-1} are the bending vibration peaks of C-N . The above analysis indicates that the designed molecule was successfully synthesized.

3.2. Effect of HPA-COOH concentration on scale inhibition

According to the national standard of People's Republic of China (GB/T 16632-2008), static scale inhibition experiments of calcium scale were conducted. The above mixtures with different concentrations of HPA-COOH were placed in an oven for 10 hours at 80 °C. The scale inhibition efficiency (η) of HPA-COOH for CaCO_3 and CaSO_4 scales and the experimental results are shown in Fig. 3. As indicated, when the HPA-COOH concentration was less than 400 mg/L, the scale inhibition efficiency increased with an increase in the HPA-COOH concentration; the scale inhibition efficiency was not significantly improved, when the HPA-COOH concentration was controlled in the range of 400 to 700 mg/L. At the concentration of 400 mg/L, the inhibition rates of HPA-COOH for CaCO_3 and CaSO_4 scales were 97.3% and 91.2%, respectively, indicating a good efficiency of scale inhibition. HPA-COOH with a three-dimensional structure exhibited an excellent chelating effect with Ca^{2+} , and the chelating effect can destroy the crystals formation of CaSO_4 and CaCO_3 [12]. In addition, the scale inhibi-

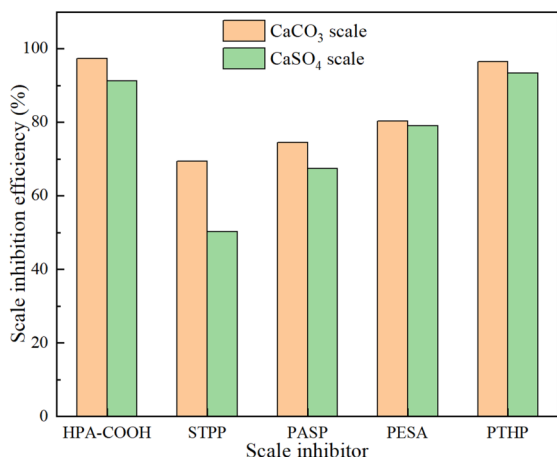


Fig. 4 Effect of different inhibitors on scale inhibition.

tion efficiency of HPA-COOH efficiency in the case of CaCO_3 was higher than that in the case of CaSO_4 .

3.3. Effect of different scale inhibitors on scale inhibition

In the static scale inhibition experiments, the above mixtures with different scale inhibitors were placed in an oven for 10 hours at 80 °C, and the concentration of the scale inhibitor was 400 mg/L. The effect of different scale inhibitors on the scale inhibition efficiency for CaCO_3 and CaSO_4 scales was evaluated, and the experimental results are shown in Fig. 4. As indicated, both HPA-COOH and PTHP inhibitors exhibited excellent efficiency and were superior to the other three scale inhibitors. A reasonable explanation for the result is that both HPA-COOH and PTHP inhibitors can form a three-dimensional structure in aqueous solution, resulting in more functional groups ($-\text{COOH}$ or $-\text{H}_2\text{PO}_3$) that can participate in the chelating effect with Ca^{2+} . In addition, such functional groups with lone pair electrons can be beneficial for enhancing the adsorption of the inhibitor at calcium deposits [13]. However, it is well known that carboxylic acids are more environmentally friendly than phosphoric acids. Therefore, the phosphorus-free scale inhibitor studied in this paper is of great significance for sustainable development. The efficiency of HPA-COOH in inhibiting scale formation was found to be higher than that of commercial scale inhibitors such as sodium triphosphate (STPP), polyaspartate (PASP) and polyepoxysuccinic acid (PESA), which promoted the development and research of highly effective water treatment agents.

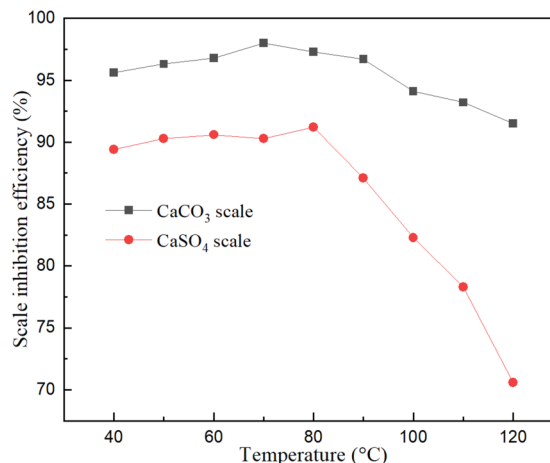


Fig. 5 Effect of holding temperature on scale inhibition.

3.4. Effect of holding temperature on scale inhibition

In static scale inhibition experiments, the above mixtures with a concentration of 400 mg/L HPA-COOH were placed in an oven for 10 hours at different temperatures. The effect of holding temperature on the scale inhibition efficiency of HPA-COOH for CaCO_3 and CaSO_4 scales was evaluated, and the experimental results are shown in Fig. 5. It was found that the holding temperature had little effect on CaCO_3 scale inhibition and had a great influence on CaSO_4 scale inhibition. The scale inhibition efficiency of HPA-COOH for CaCO_3 and CaSO_4 scales remained almost constant when the holding temperature was controlled in the range of 40 to 80 °C; when the holding temperature exceeded 90 °C, the scale inhibition efficiency gradually decreased with increasing holding temperature. There are two reasonable explanations for this result. First, with an increase in the holding temperature, the carboxyl groups in the molecule undergo esterification, resulting in a reduction in the carboxyl group, which may weaken the scale inhibition efficiency [16]. Second, an increase in the holding temperature reduces the effective adsorption of scale inhibitor on calcium deposits, which leads to a decrease in the scale inhibition rate. Even if the holding temperature exceeds 110 °C, the inhibition rates of HPA-COOH for CaCO_3 and CaSO_4 scales were still greater than 90% and 70%, respectively. The analysis of the results showed that HPA-COOH had excellent scale inhibition efficiency and temperature resistance.

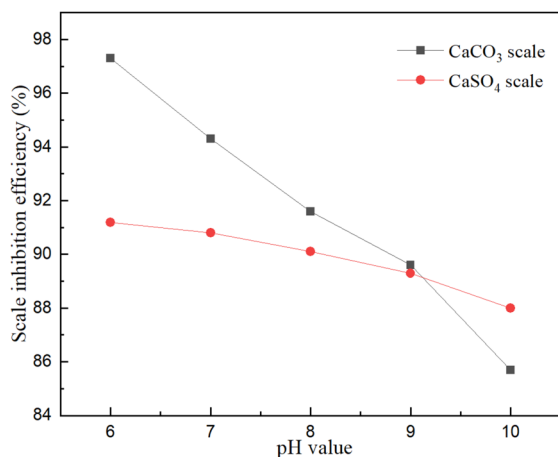


Fig. 6 Effect of pH value on scale inhibition.

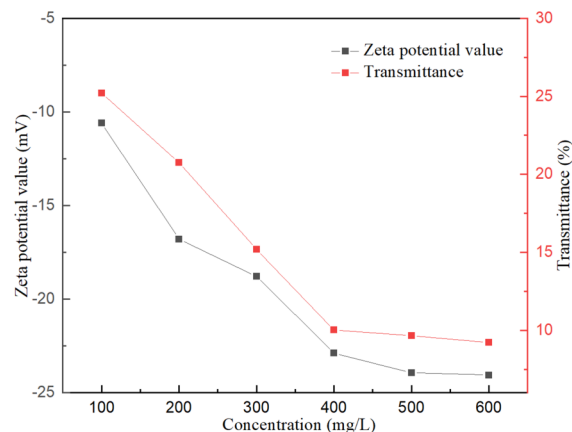
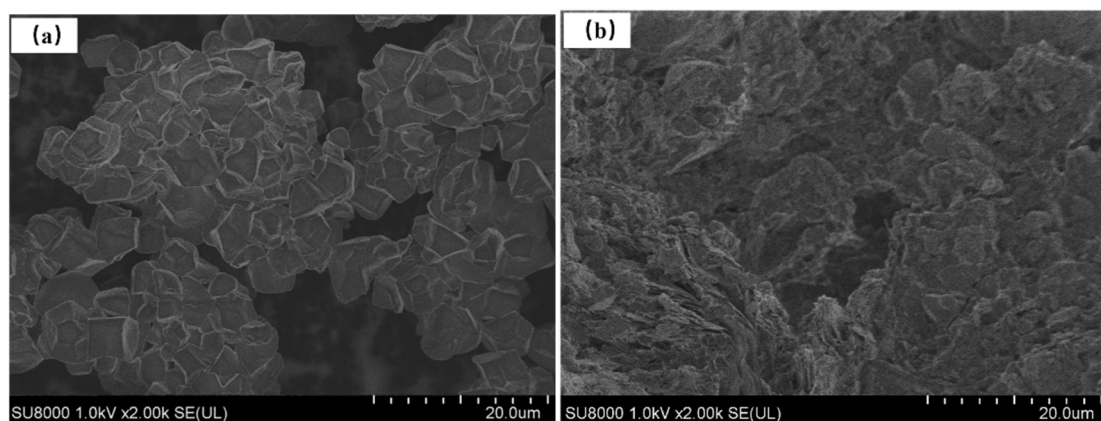


Fig. 7 Dispersion test of HPA-COOH.

Fig. 8. SEM images of CaCO₃ scale a) initial; b) with 400 mg/L HPA-COOH.

3.5. Effect of pH value on scale inhibition

In static scale inhibition experiments, the pH of the above mixtures with a concentration of 400 mg/L HPA-COOH was adjusted by sodium hydroxide, and the mixtures were placed in an oven for 10 hours at 80 °C. The effect of the pH value on the efficiency of HPA-COOH for inhibition of CaCO₃ and CaSO₄ scales was evaluated, and the experimental results are shown in Fig. 6. It was found that the pH value had little effect on the efficiency of HPA-COOH in inhibiting CaSO₄ scale. Meanwhile, it was easily found that the scale inhibition efficiency of HPA-COOH for CaCO₃ gradually decreased as the pH value increased. There are two reasonable explanations for this phenomenon. First, an increase in the OH⁻ concentration can convert bicarbonate to carbonate, resulting in the rapid growth of CaCO₃ scale crystals. Second, with an increase in the pH value, OH⁻ first reacted with Ca²⁺ to form a slightly soluble precipitate such as Ca(OH)₂, which may hinder the adsorption of the hyperbranched polymeric

scale inhibitor on the surface of CaCO₃ crystals [18]. In general, the hyperbranched polymer has stable scale inhibition and alkaline resistance.

3.6. Dispersion properties of scale inhibitors

The effect of different concentrations of HPA-COOH on dispersion performance of iron oxide was evaluated, and Fig. 7 shows the transmittance and the zeta potential value of the iron mixture. It was found that the transmittance of the iron mixture decreased gradually with the increase of the scale inhibitor content, indicating that a finer and more stable calcium scale is formed in the solution and the dispersability of the scale inhibitor is improved. In addition, the absolute value of the zeta potential increased gradually with the increase of the scale inhibitor content. The carboxyl groups grafted at the end of the hyperbranched molecular structure repelled each other under electrostatic interaction, which easily led to the formation of a double electron layer structure, making the

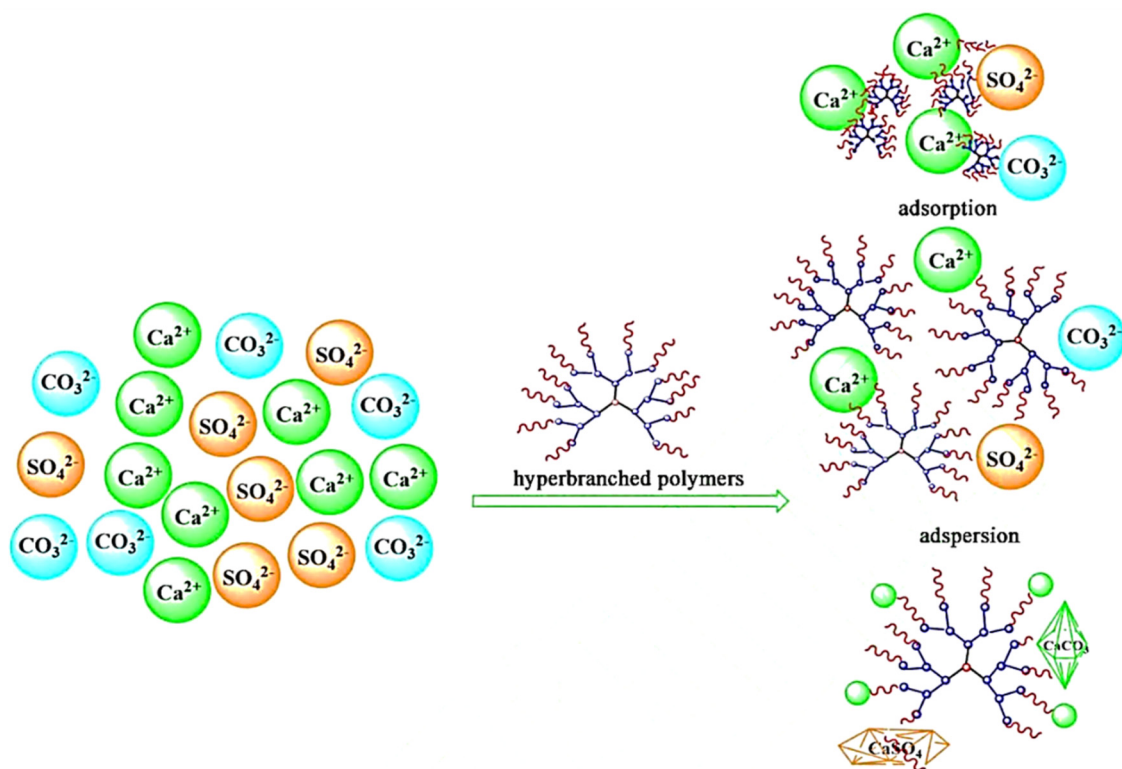


Fig. 9 Schematic diagram of scale inhibition mechanism of HPA-COOH.

hyperbranched polymer easier to disperse. The low transmittance and zeta potential can effectively prevent the deposition of calcium scale.

3.7. SEM analysis on CaCO_3 scale

The SEM images of CaCO_3 scale are shown in Fig. 8. As indicated, without scale inhibitor, the surface of CaCO_3 scale crystal was smooth and has a regular rectangular shape and a dense structure, showing the calcite type. With 400 mg/L HPA-COOH, the surface of the CaCO_3 scale crystals exhibited a large number of honeycomb defect holes, and the growth of the CaCO_3 scale crystals was disorderly and loose, forming a large and unstable crystalline form and resulting in a change in the crystal form of the CaCO_3 scale. Complete crystal formation was hampered due to the superior scale inhibition efficiency.

3.8. Scale inhibition mechanism

Fig. 9 shows the mechanism of inhibition of CaCO_3 and CaSO_4 scales by HPA-COOH. The hyperbranched polymeric inhibitor (HPA-COOH) dispersed around the scale ions and wrapped the formed calcium scale crystals to form a double electric layer structure, which facilitated scale dispersion and inhibition. In addition, due to the high negative charge den-

sity of the oxygen atom in the grafted carboxylic acid group, HPA-COOH was easy to interact with Ca^{2+} in the scale crystal, enhancing the adsorption behavior on the crystal surface, which resulted in crystal distortion.

4. Conclusions

1) The inhibition rates of HPA-COOH for CaCO_3 and CaSO_4 scales exceeded 90%, exhibiting the excellent inhibition efficiency of calcium scales. The scale inhibitor (HPA-COOH) with a three-dimensional structure exhibited excellent chelating effect with Ca^{2+} . Due to the high negative charge density of the oxygen atom in the grafted carboxylic acid group, HPA-COOH was easy to interact with Ca^{2+} in the scale crystal, enhancing the adsorption behavior on the crystal surface, which resulted in crystal distortion.

2) The scale inhibition performance of HPA-COOH without phosphorus was found to be higher than that of commercial scale inhibitors, which facilitated the development and research of highly efficient and environmentally friendly water treatment agents.

References

1. S.P. Gopi, V.K. Subramanian, K. Palanisamy, *Ind. Eng. Chem. Res.*, **54**, 3618, 2015. <https://doi.org/10.1021/ie5034039>
2. A. Valiakhmetova, K.S. Sorbie, L.S. Boak, S.S. Shaw, *SPE Prod. Oper.*, **32**, 343, 2017. <https://doi.org/10.2118/178977-PA>
3. M.F. Mady, A.T. Abdelaal, A. Moschona, K.D. Demadis, *Energy Fuels*, **37**, 4365, 2023. <https://doi.org/10.1021/acs.energyfuels.2c04277>
4. M.F. Mady, S. Abdel-Azeim, M.A. Kelland, *Ind. Eng. Chem. Res.*, **60**, 12175, 2021. <https://doi.org/10.1021/acs.iecr.1c02441>
5. M.F. Mady, M.A. Kelland, *Energy Fuels*, **31**, 4603, 2017. <https://doi.org/10.1021/acs.energyfuels.7b00708>
6. R.W.P. Ortiz, J. Oliveira, G..V. Vaz, N. Passos, *SPE J.*, **29**, 1, 2023. <https://doi.org/10.2118/218011-PA>
7. M.S.H. Bader, *J. Petrol. Sci. Eng.*, **55**, 93, 2007. <https://doi.org/10.1016/j.petrol.2006.04.010>
8. S. Elkatatny, M. Mahmoud, B. Bageri, *J. Pet. Explor. Prod. Technol.* 2018, **8**, 165, 2018. <https://doi.org/10.1007/S13202-017-0319-1>
9. F. Jones, P. Jones, M.I. Ogden, W.R. Richmond, A.L. Rohl, M. Saunders, *J. Colloid Interf. Sci.*, **316**, 553, 2007. <https://doi.org/10.1016/j.jcis.2007.09.005>
10. H.J. Bemelaar, A.H. Nasr-El-Din, A.C.D. Wolf, N.J. LePage, *SPE J.*, **16**, 559, 2011. <https://doi.org/10.2118/127923-PA>
11. M.F. Mady, A. Rehman, M.A. Kelland, *Ind. Eng. Chem. Res.*, **60**, 8331, 2021. <https://doi.org/10.1021/acs.iecr.1c01473>
12. H. Huang, Q. Yao, B. Liu, N. Shan, H. Chen, *New J. Chem.* 2017, **41**, 12205, 2017. <https://doi.org/10.1039/C7NJ02201H>
13. M. Yan, Q. Tan, Z. Liu, H. Li, Y. Zheng, L. Zhang, Z. Liu, *ACS Omega* 2020, **5**, 15487, 2020. <https://doi.org/10.1021/acsomega.0c01620>
14. M.K.Jensen, M.A. Kelland, *J. Petrol. Sci. Eng.*, **94**, 66, 2012. <https://doi.org/10.1016/j.petrol.2012.06.025>
15. Y. Wang, H. Chen, Z. Zhang, H. Huang, B. Liu, K. Ding, *J. Appl. Polym. Sci.* **136**, 48041, 2019. <https://doi.org/10.1002/app.48041>
16. M.F. Mady, P. Charoensumran, H. Ajiro, M.A. Kelland, *Energy Fuels*, **32**, 6746, 2018. <https://doi.org/10.1021/acs.energyfuels.8b01168>
17. K. Popov, M. Oshchepkov, S. Kamagurov, S. Tkachenko, J. Dikareva, G.. Rudakova, *J. Appl. Polym. Sci.*, **134**, 45, 2017. <https://doi.org/10.1002/app.45017>
18. H. Huang, Q. Yao, Q. Jiao, B. Liu, H. Chen, *J. Saudi Chem. Soc.*, **23**, 61, 2019. <https://doi.org/10.1016/j.jscs.2018.04.003>