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Novel single agent of imidazoline - phosphate copolymer with excellent corrosion and scale inhibition effect for wells flooded by CO_2 (ICCUSC2023)

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ABSTRACT

Water-alternating-gas injection of CO_2 flooding has received attention as a proven gas channeling controlling method for enhancing oil recovery. However, the application of this method led to the coexistence of corrosion and scaling, affecting well productivity. Current single agent has slight anti-corrosion effect, which mainly concentrates on scale prevention. Meanwhile, the treatment means of agent compounding has poor compatibility. Therefore, developing a single agent with both anti-scale and anti-corrosion properties is beneficial to production. In this study, the dehydrated product of cyclization of amine and acid were condensed with aldehydes and ketones under acidic conditions to prepare mannich base imidazoline groups, that could play the corrosion inhibition effect. The imidazoline - phosphate copolymer was synthesized by introducing the scale inhibition of phosphate esters into imidazoline, followed by a grafting reaction. Corrosion and scale inhibition properties of the synthesized agent were evaluated by rotary hanging weight loss method, and the biodegradable performance was analyzed. The results of infrared spectrum characterization illustrated the successful binding between the effective functional groups of imidazoline groups and phosphate groups. The scale inhibition rate of 30 mg/L of the synthesized agent to calcium carbonate ($CaCO_3$) was 92.41%. The corrosion rate of CO_2 on steel was 0.061 mm/a when the synthesized agent was added, indicating that the corrosion resistance of the imidazoline - phosphate copolymer was superior than that of most of the reported single agent used for corrosion inhibition and scale inhibition. The chemical oxygen demand of the synthesized agent decreased significantly when aging in the soil where plants grew, and the biodegradation rate of the synthesized agent at 28 days was 70.93%. The single agent of imidazoline - phosphate copolymer exhibited superior performance in solving the problems of corrosion and scaling in the wellbore, which could facilitate the application of captured and buried CO2 in oil displacement, so that meeting the requirements of environmental protection and efficient reservoir development.

Keywords: Water-alternating-gas injection, carbon dioxide utilization, anti-corrosion agent, scale remover, imidazoline - phosphate copolymer

NONMENCLATURE

Abbreviations	
APEN	Applied Energy
Symbols	
n	Year

1. INTRODUCTION

With the development of conventional reservoir, heterogeneous reservoirs have become the main objects of exploitation and development [1]. Carbon dioxide (CO_2) flooding is an effective means to replenish energy for low permeability reservoirs, which greatly contribute to utilize captured and buried CO_2 [2]. However, when CO_2 is injected continuously, it breaks through prematurely. As a result, the measure of water-alternating-gas injection of CO_2 flooding has been proposed [3]. As a method that combines the advantages of water flooding and gas flooding, it is one of the important means to control gas channeling to enhance oil recovery. Nevertheless, the wide application of water-alternating-gas injection led to the problems of corrosion and scaling [4]. The coexistence of corrosion and scaling

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leads to fracture of pipes, which seriously affects the productivity of oil well.

Scale removers and corrosion inhibitors are applied to scaled oil wells to solve this problem [5]. The corrosion inhibitor and scale remover used on site are two kinds of agents. Whether adding a single corrosion inhibitor or a single scale remover, it is mainly effective in scale inhibition, while the anti-corrosion effect is always weak. In order to take into account both the effects of corrosion inhibition and scale inhibition, the compound of corrosion inhibitor and scale remover has been injected into the oil wells simultaneously, however, there always lies a compatibility contradiction between the two agents and the formation [6]. In addition, the injection technology of this means of agent compounding is complicated. There has been no research on integrated agents so far, which cannot meet the requirements of oil well productivity protection when scaling and corrosion coexist [7]. Therefore, it is necessary to develop a single agent with both great anti-scale and excellent anti-corrosion properties.

Herein, a single agent of imidazoline - phosphate copolymer was synthesized. The first step was the preparation of the mannich base imidazoline group which play the role of corrosion inhibition. Then the imidazolin-phosphate copolymer was synthesized by grafting the scale inhibition group of phosphate into imidazoline. The rotary hanging weight loss method was used to study the corrosion inhibition and scale inhibition properties of the synthesized single. The chemical oxygen demands were tested to evaluate the biodegradable performance of the imidazoline - phosphate copolymer. The development of this single agent is equivalent to forming a multifunctional formulation with anticorrosion and scale inhibition. The application of this single agent can address the worries of implementing the measure of water-alternating-gas injection of carbon dioxide (CO_2) flooding, providing guidance for further optimization of capture, utilization and storage of carbon.

2. MATERIAL AND METHODS

2.1 Preparation of single agent of imidazoline - phosphate copolymer

By molecular structure design, the synthesis route of the copolymer mainly includes the preparation of mannich base imidazoline and the grafting reaction. The preparation of mannich base imidazoline can be divided into following two steps. The first step is the amidation of amine with acid to form an intermediate. Then the second step that the intermediate was dehydrated and condensed with aldehydes and ketones can be conducted to synthesize mannich base imidazoline group. The grafting reaction refers to introducing the phosphate ester group into imidazoline to obtain the single agent of imidazoline - phosphate.

2.2 Static anti-scaling performance test

The synthesized imidazoline - phosphate copolymer was formulated into a 1000 mg/L solution. $CaCl_2$ solution with the concentration of 11.09 g/L and Na_2CO_3 solution with the concentration of 11.10 g/L were also prepared. Then 200 mL of ultra-pure water was added to each of 3 volumetric bottles respectively.

For the first volumetric bottle, 6 mL of $CaCl_2$ solution and 6 mL of Na_2CO_3 solution was added to the original 200 mL of ultra-pure water. Ultra-pure water was then added to the first bottle until the total volume of the solution reached 250 mL. The solution in the first bottle that had been formulated without scale inhibitor was labeled as blank control 1. In the second bottle, only 7.5 mL of the formulated scale inhibitor solution was added and then water was added until the solution volume was 250 mL, without adding Na_2CO_3 and $CaCl_2$. The solution in the second bottle was labeled as blank control 2. In the third bottle, 7.5 mL of scale inhibitor solution, 6 mL of Na_2CO_3 and 6 mL of $CaCl_2$ were added, and then water was added to bring the total solution volume to 250 mL. The solution in the 3rd bottle was seen as the experimental group. All the concentrations of synthesized agent in these three bottles were 30 mg/L.

These three bottles were placed in a 50 ℃ water bath for 16 hours, and then taken out and cooled until the bottles came to room temperature. 25 mL of supernatant was taken from each of the three bottles and titrated with 0.005 mol/L of EDTA standard solution. The scale inhibition rate of the synthesized imidazoline - phosphate copolymer to $CaCO_3$ was calculated using the following equation [8].

$$S = \frac{V_e - V_1}{V_2 - V_1} \times 100\%$$

Where V_e, V_1 and V_2 are the volume of EDTA standard solution consumed by titrating the concentration of Ca^{2+} in the experimental group, blank control 1 and blank control 2, respectively.

2.3 Rotary coupon corrosion test

The corrosion efficiency of CO_2 on steel in the presence of the synthesized agent was evaluated by the method of rotating weight loss. The steel sheet with the mass of *m* was hung into the oil field production water with or without corrosion inhibitor, soaked for 5 days under the 60 ℃, and then the test sheet was taken out. After cleaning and drying, the mass of the steel sheet was weighed and recorded as m_1. The corrosion rate was calculated using the following equation [9].

$$r = \frac{8.76\times104\times(m-m_1)}{S\cdot t\cdot\rho}$$

Where S is the total area of the steel sheet, cm^2; ρ is the density of the steel sheet, g/cm^3; t is the testing time, h.

Scanning electron microscope (SEM) was used to observe the corrosion morphology of steel surfaces with and without the addition of the imidazoline - phosphate copolymer, so that the corrosion inhibition effect of the synthesized agent was demonstrated from the macroscopic perspective.

2.4 Evaluation of biodegradability of the synthesized single agent

The aerobic biological method was used to degrade the synthesized imidazoline - phosphate copolymer. The biodegradability of the single agent was evaluated by measuring the degradation rate of chemical oxygen demand (COD). The compositions of the simulated salt solutions required by the experiment were shown in Table 1. The oil-free air pump was used to aerate 1 L ultra-pure water for 8h until the dissolved oxygen (DO) in the water reached 8 mg /L. Then 1 mL of calcium chloride ($CaCO_3$) solution, 1 mL of ferric chloride ($FeCl_3$) solution, 1 mL of magnesium sulfate ($MgSO_4$) solution and 1 mL of phosphate buffered solution were added to the 1 L water with DO, respectively, so that the diluent was obtained.

Table 1 The composition of simulated salt solution

Number	Name	Composition	Concentration / （$mg\cdot L^{-1}$）
1	$CaCO_3$ solution	$CaCO_3$	27.5
2	$FeCl_3$ solution	$FeCl_3\cdot 6H_2O$	0.25
3	$MgSO_4\cdot$ solution	$MgSO_4\cdot 7H_2O$	22.5
4	Phosphate buffered solution	KH_2PO_4	8.5
		K_2HPO_4	33.4
		NH_4C1	1.7

100 g of plant growing soil was added into 1 L of water, and the supernatant was taken as the inoculum, which referred to the aging environment of the synthesized agent after being fully stirred and left for 10 min. The synthesized imidazoline - phosphate copolymer was added to a serum bottle containing 30 mL of inoculum and 270 mL of diluent. Both the synthesized group and the blank control group were aged at 30 ℃ for 28 days, and the changes of the COD content of solution in serum bottle were measured every 7 days. The biodegradation rate of the synthesized imidazoline - phosphate copolymer was calculated using the following equation [10].

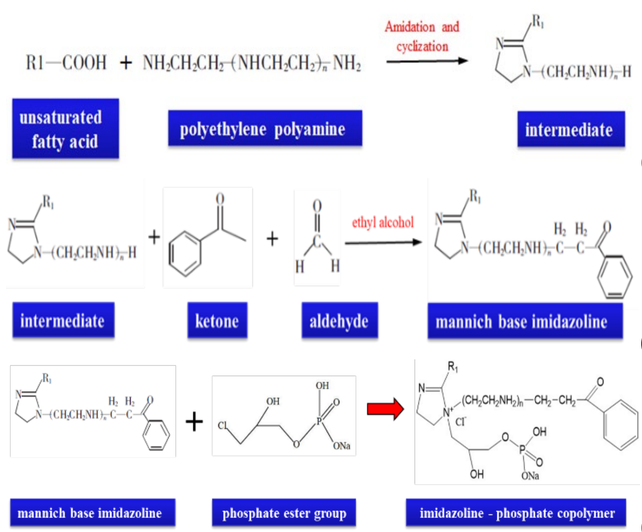
$$B= (1 - \frac{C_t - C_{bt}}{C_0 - C_{b0}}) \times 100\%$$

where B is the biodegradation rate the sample; C_t and C_0 are COD content in the solution containing copolymer at time t and at initial time, respectively; C_{bt} and C_{b0} are COD content of the blank control group at time t and at initial time, respectively.

3. RESULTS

3.1 Synthesis of the single agent

The mannich base imidazoline group, which acted as a corrosion inhibitor, was obtained by the routes shown in the chemical equation 1 and 2. Then the grafting reaction of the introduction of the scale inhibition group of phosphate ester into the synthesized mannich base imidazoline with was drawn in the chemical equation 3. Both anti-corrosion groups and anti-scale groups were present in this agent, so that the application of the synthesized single agent could achieve both effects.



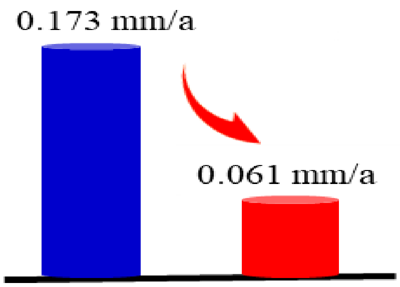
(1)
(2)
(3)

3.2 Scale inhibition ability

Both imidazoline groups and phosphate groups existed in the synthesized imidazoline - phosphate copolymer. The scale inhibition rate of 30 mg/L of the synthesized agent of imidazoline - phosphate copolymer to calcium carbonate ($CaCO_3$) was 92.41%, indicating that the reaction between Ca^{2+} and CO_3^{2-} could be effectively inhibited by adding this single agent to the solution before precipitating.

3.3 Corrosion inhibition ability

The imidazoline group successfully introduced into the single agent reduced the corrosion rate of the metal in the presence of carbon dioxide. As shown in Figure 1, the corrosion rate of pipe string in corrosive environment under CO_2 condition without adding scale inhibitor was 0.173 mm/a, which did not meet the standards of oil and gas industry. After adding the synthesized copolymer, the corrosion rate of the steel decreased to 0.061 mm/a due to the adsorption effect of imidazoline group in the single agent.

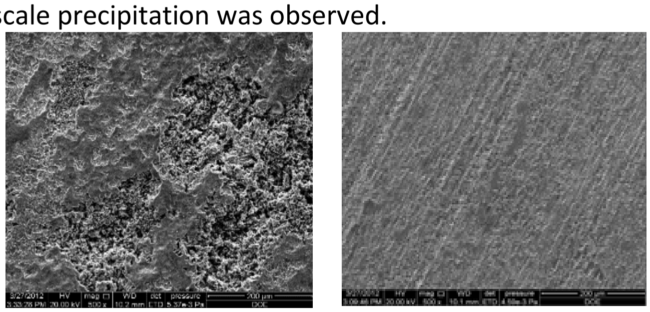


(a) no corrosion inhibitor (b) with the synthesized copolymer

Fig. 1. Corrosion rate comparison

3.4 SEM results

The inhibition capacity of corrosion and scale of the imidazoline - phosphate copolymer was further analyzed by the results of SEM. It was seen from Figure 2a that the corrosion and scaling condition on the surface of the steel sheet in the simulated water without the addition of imidazoline - phosphate copolymer was relatively serious. In addition, some obvious corrosion pits could be observed, and a large number of scale samples were attached to the surface of the steel sheet. The surface morphology of the steel sheet after adding the single agent was illustrated in Figure 2b. The corrosion on the surface of the steel sheet was uniform, and no obvious scale precipitation was observed.



(a) without scale remover or corrosion inhibitor (b) with the synthesized copolymer

Fig. 3. SEM morphology of steel sheet after corrosion in simulated water

3.5 Biodegradability of the synthesized single agent

It was seen from Figure 3 that the biodegradation rate of the imidazoline - phosphate copolymer increased significantly with the aging time. The biodegradation rate of the copolymer could reach more than 30% after 7 days of aging and the final biodegradation rate at 28 days was 70.93%.

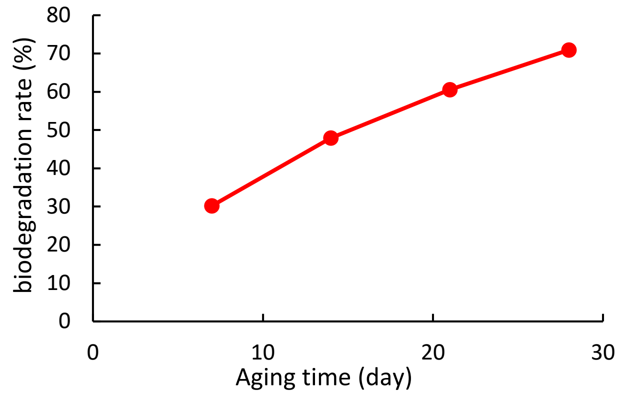


Fig. 3. Biodegradability of the copolymer

4. DISCUSSION

The addition of the novel single agent of imidazoline - phosphate copolymer led to an obvious decrease in the scaling phenomena, indicating that the chelation efficiency between this single agent and calcium ions was relatively high, effectively reducing the concentration of calcium ions in the liquid phase [11]. Moreover, the addition of this agent could provide a large steric hindrance, phosphate groups contained in the synthesized imidazoline - phosphate copolymer disturbed the process of crystal aggregation and ordering through threshold effect, so as to change the morphology of crystal nucleus and inhibit nucleation of calcium scale. The particles formed in the nucleation stage were adsorbed and the thermodynamic stability of nucleation was disrupted, thus preventing the growth process of crystal. The morphology of calcium carbonate crystal was changed under the action of the synthesized imidazoline - phosphate copolymer, making the calcium scale easier to be removed.

The change in the corrosion rate could be explained that a protective layer composed of imidazoline hydrophobic groups was formed outside the surface of the sheet steel, which prevented the contact between the corrosive medium and the metal surface, so as to reduce the corrosion rate of the metal. Imidazoline group could prevent the corrosion of metal materials caused by dissolved oxygen and acid gas in corrosive media by covering effect and increasing the activation energy of corrosion reaction [12]. At the same time, the mannich base imidazoline realized the bonding of two nitrogen atoms on the imidazoline molecular ring with iron atoms on the metal surface through the coordination of unbonded lone pair electrons on the polar amino nitrogen atom to the sheet steel.

The results of SEM showed that the synthesized imidazoline - phosphate copolymer could generate a complete protective film on the steel surface, demonstrating the effective cooperation between the corrosion inhibition group and the anti-scale group. The imidazoline group played a synergistic role with the phosphate group to inhibit the corrosion and scaling of the steel sheet in simulated water.

In order to guarantee the environmental protection performance of this synthesized single agent, it was necessary to evaluate its biodegradability. The conclusion that synthesized single agent of imidazoline - phosphate copolymer was easy to biodegrade and had little environmental pollution could be drawn. The application of this single agent can meet the multiple requirements of efficient corrosion, scale inhibition and environmental protection. The development of imidazoline - phosphate copolymer has been realized from the perspective from molecular designing, which can satisfy the requirement that single agent has multiple functions.

5. CONCLUSIONS

In this study, a novel single agent of imidazoline - phosphate copolymer with excellent corrosion and scale inhibition effect was successfully synthesized by introducing the scale inhibition of phosphate esters into mannich base imidazoline. The

experimental results showed that the single agent of imidazoline - phosphate copolymer facilitated the adsorption on the metal material, accounting for significantly improving the Corrosion inhibition ability and scale inhibition ability. The scale inhibition rate of the synthesized single agent to CaCO3 was 92.41% and the corrosion rate on steel was 0.061 mm/a in the presence of CO_2. The biodegradation rate of the synthesized single agent at 28 days was 70.93%, indicating that the agent was environmentally friendly. These results indicated that the performances of the imidazoline - phosphate copolymer were superior than that of most of the reported single agent used for corrosion inhibition and scale inhibition. The novel single agent of imidazoline - phosphate copolymer has a good ability to solve the problem of the coexistence of corrosion and scaling for practical applications of water-alternating-gas injection of CO_2. The development and promotion of this single agent of imidazoline - phosphate copolymer provide basic guarantee for carbon capture, utilization and storage.

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DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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