

Calcium carbonate scale inhibition of a cathode surface under polarization by 2-phosphonobutane-1,2,4-tricarboxylic acid

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Received 13 January 2020; Accepted 7 September 2020

ABSTRACT

Scale formation on the cathode surface of an electrocatalytic oxidation equipment restricts the effective operation of the equipment. The scaling mechanism on a cathode surface and the scale inhibition performance of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) under cathodic polarization were studied by gravimetric, solution, and surface analysis methods. The results showed that the amount of scaling on the cathode surface increased as the polarization potential shifted negatively. The scale inhibition performance of PBTCA was enhanced with the increase of PBTCA concentration. However, when the polarization potential was negatively shifted to -1.3 V and below, the addition of PBTCA at lower concentrations promoted scaling on cathode surface. The CaCO_3 crystals formed in the blank solution were mainly calcite, with some vaterite possibly caused by electric field. In contrast, all the CaCO_3 crystals formed on cathode surface in solution containing PBTCA were calcite. The addition of PBTCA increased the Ca^{2+} concentration and pH in solution near the cathode surface. The promotion of scaling with lower concentration PBTCA was mainly attributed to the higher pH of the solution and the weak solubilization of the scale inhibitor.

Keywords: Cathodic polarization; Calcium carbonate scaling; 2-phosphonobutane-1,2,4-tricarboxylic acid; Cathode scale inhibition; Hydrogen evolution

1. Introduction

The scaling phenomenon is highly likely to occur in water-based heat exchange systems, such as boiler systems with poor water quality and various types of cooling water systems [1,2] in various industries, such as the petrochemical, electric power, and steel production industries. Due to the continuous evaporation and concentration of the water solution, the dissolved ion concentration in the water increases, causing the deposition of insoluble salts such as carbonates and sulfates on the heat exchange surface, which reduces the heat exchange capacity of the system [3,4]. In recent years, membrane technology has been widely used in the field of water treatment [5,6]. The scaling on the

membrane surface has also become one of the main problems affecting the operation of the system due to the concentration of water [7,8]. In particular, with the application of electrochemical technology in environmental treatment, scaling on the cathode surface of electrocatalytic oxidation equipment has also attracted the attention of researchers [9,10].

Significant research on scale inhibition methods has been focused on cooling water systems [11]. There are some effective scale inhibition methods used in cooling water systems, including the use of chemical scale inhibitors and physical scale inhibition such as low-voltage electronic scale inhibition, electromagnetic and ultrasonic wave scale inhibition, high-voltage electrostatic scale inhibition, and

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so on [12–15]. These methods are mainly applied in heat exchange systems [16,17]. The addition of a chemical scale inhibitor is the most widely-used scale inhibition method in industrial applications. A series of chemical scale inhibitors have been developed and the mechanism of scale inhibition has also been researched in depth. The development of green scale inhibitors is a current direction of scale inhibitors and has been applied in practice [18–20]. It has not been reported that scale inhibitors can be used in electrocatalytic cathode scale inhibition. If a low concentration of a green scale inhibitor could be used to control the scale of the cathode, the secondary pollution to the water should be small due to the low concentration of the introduced scale inhibitor. In the process of electrocatalysis as a biochemical pretreatment, a small amount of introduced scale inhibitor could be used as organic matter to provide carbon and nitrogen sources for the subsequent biochemical treatment [21].

The cathodic polarization process of some electrochemical devices in industry often promotes the scaling on the cathode surface. For example, in the practical application of electrocatalytic oxidation treatment of organic wastewater, the main problem is the failure of the electrode [9,10], including anodic oxidation and cathode scaling, which greatly reduces the degradation efficiency of the equipment after a short period of time and seriously affects the normal operation of the equipment. The problem of anode failure can be overcome by the selection of suitable anode materials [22,23]. However, there is currently no effective control method for the problem of cathode scaling. Generally, there is a certain concentration of hardness (Ca^{2+} and Mg^{2+}) and alkalinity (HCO_3^-) in wastewater. During the operation of the electrocatalytic equipment, the hydrogen evolution reaction at the cathode causes the rise of the pH of the liquid layer on the cathode surface [24], resulting in precipitation of deposits, such as calcium salts, on the cathode surface. At present, the commonly used methods to remove the surface scale on the cathode include mechanical cleaning, pole inversion, ultrasonic cleaning, chemical cleaning, manual erasing, and so on [25]. All these methods are to remove the scale that has already formed on the cathode surface. The equipment needs to stop running when descaling. For some wastewater that is prone to scaling, the cycle time of cathode is very short (1–2 d or less). The equipment needs frequently shutting down and descaling. Therefore, it is necessary to find an efficient and low-cost method to suppress the fouling of the cathode plate during operation of the electrocatalytic equipment.

This paper takes 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCa) as an example to study the scale inhibition performance and characteristics of a scale inhibitor under cathodic polarization conditions and discusses the feasibility of a scale inhibitor applied to cathodic scale inhibition. PBTCa is an ultra-low phosphorus organic phosphonate scale and corrosion inhibitor that developed and applied by Geffers and Radt [26] in Germany in the early 1970s. Its phosphorus content is lower than 11.5% [27]. PBTCa contains one phosphonic acid group ($-\text{PO}_3\text{H}_2$) and three carboxylic acid groups ($-\text{COOH}$). In neutral and weak alkaline water solutions, PBTCa exists in the form of ions, in which $-\text{PO}_3\text{H}^-$ and $-\text{COO}^-$ can form ionic bonds with Ca^{2+} to achieve the purpose of scale inhibition [28,29].

2. Materials and methods

2.1. Experimental medium

The scaling solution containing 6 mmol/L CaCl_2 and 12 mmol/L NaHCO_3 was prepared according to the national standard of China numbered GB/T 16632-2008. A non-scaling solution containing 6 mmol/L NaCl and 12 mmol/L NaHCO_3 was prepared as a contrast. All the chemicals used were analytically pure (AR) and all test solutions were prepared with deionized water. PBTCa was provided by the Shanghai DuoJia Water Treatment Company, (Shanghai, China). The structural formula of PBTCa is shown in Fig. 1.

2.2. Scale inhibition experiment on cathode surface

The surface scale inhibition test was carried out under cathodic polarization with a potentiostat. The experimental device is shown in Fig. 2. The material of the working electrode was 316 stainless steel with dimensions of 20 mm × 50 mm × 2 mm and a total effective working area of 18 cm². The auxiliary electrode was a platinum plate and the reference electrode was a saturated calomel electrode (SCE). The stainless steel was grinded with emery papers from 500 to 1,500 mesh and then cleaned in sequence with 10% HNO_3 solution, 0.5 mol/L NaOH solution, and deionized water before each test.

The scale forming experiments were carried out on a stainless steel cathode by applying different polarization potentials in the range of -1.0 to -1.5 V. The stainless steel cathode was weighed before and after the experiment. The increase in the weight of the stainless steel during the experiment was the amount of scale formed on the cathode surface (the weight of the stainless steel cathode did not change during the experiment). The surface scale inhibition efficiency η_s was calculated as follows:

$$\eta_s = \frac{\Delta m_1 - \Delta m_2}{\Delta m_1} \times 100\% \quad (1)$$

where Δm_1 is the weight increase of the stainless steel cathode after the experiment in the scaling solution with no additives and Δm_2 is the weight increase of the stainless steel cathode after the experiment in the scaling solution with the scale inhibitor.

2.3. Analysis of solution near cathode surface

In the first hour of the cathodic polarization, a 1 mL water solution was sampled every 10 min at each of the

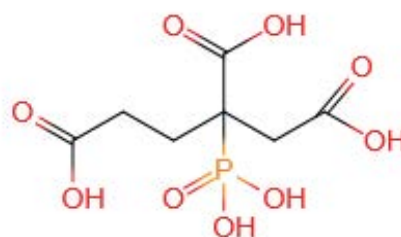


Fig. 1. Structural formula of PBTCa.

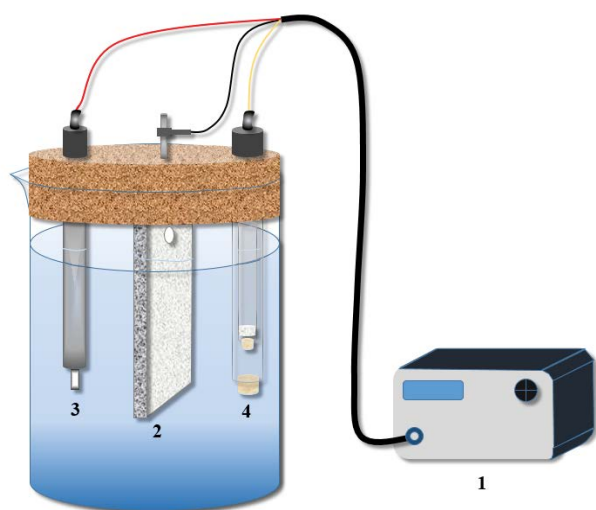


Fig. 2. Experimental device for scale inhibition on cathode surface (1) potentiostat, (2) stainless steel cathode, (3) platinum electrode, and (4) SCE.

upper and lower two different positions on cathode surface using a pipette. The sampling position was about 1 mm away from the cathode surface. All 12 mL samples were mixed together, filtered, and then measured pH. The calcium ion concentrations in the filtrate were determined by titration of disodium edetate (EDTA) standard solution according to GB/T 15452-2009.

2.4. Cyclic voltammetry measurement

The sheet of 316 stainless steel was cut into pieces of 10 mm × 10 mm × 2 mm. One side of 10 mm × 10 mm was taken as the working surface, a wire was soldered on the back of the working surface and all the non-working surfaces were enclosed with epoxy resin. The cyclic voltammetry was carried out on an electrochemical workstation CHI660E. The scanning speed was 100 mV/s.

2.5. Analysis of morphology and structure of scale formed on cathode surface

The scale formed on the stainless steel cathode was dried and its surface morphology was observed by scanning electron microscopy (SEM) (JSM-7800F). The crystal structure and type of the scale was analyzed by Fourier transform infrared (FTIR) spectroscopy (spectrum two) (FTIR-8400 S, Shimadzu Co., Ltd., Japan) and X-ray diffraction (XRD) (D8 ADVANCE, Germany).

3. Results and discussion

3.1. Scale inhibition of PBTCa on cathode surface

Fig. 3 shows the change of scale amount on the cathode surface with polarization potential under different PBTCa concentrations in the scaling solution. It can be seen that the amount of scale on the cathode surface increased with the negative shift of the polarization potential in all solutions.

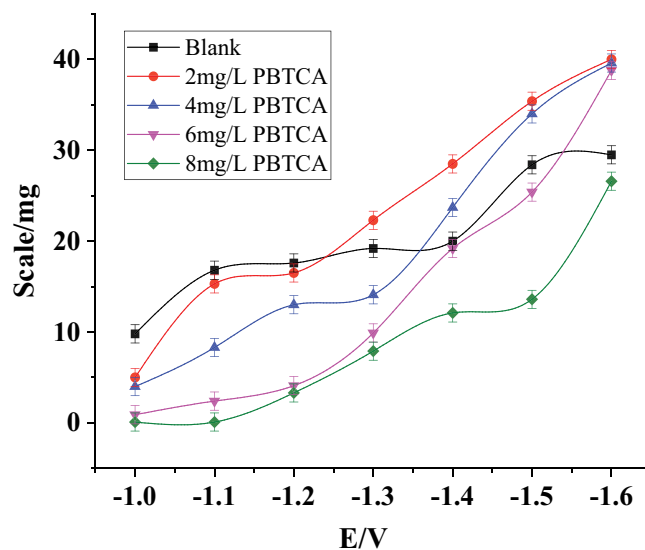
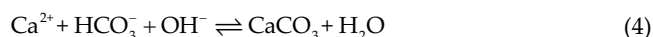


Fig. 3. Change of scale amount on cathode surface with PBTCa concentration at different polarization potentials.

The hydrogen evolution reaction mainly occurs on the cathode surface at a negative polarization potential and the H^+ ions comes from the electrolytic reaction of water:



The occurrence of the hydrogen evolution reaction increases the pH of the solution near the cathode surface and promotes the scaling reaction:



With the negative shift of the cathodic polarization potential, the rate of hydrogen evolution reaction (3) on the cathode surface increases, which further increases the pH value of the solution near the cathode surface and promotes reaction (4) to proceed rapidly toward the direction of calcium carbonate formation, resulting in an increase of the scale amount attached on the cathode surface. Fig. 3 also shows that the amount of scale on the cathode surface decreases with increasing PBTCa concentration at the same polarization potential. PBTCa is a solubilizing scale inhibitor that can chelate with Ca^{2+} to inhibit the progress of reaction (4). The higher the concentration of PBTCa, the more the sites chelate with Ca^{2+} , and the better the scale inhibition.

Table 1 shows the scale inhibition efficiency of PBTCa at various concentrations under different polarization potentials. Compared with the blank solution, the addition of PBTCa at all concentrations used in this study has a scale inhibition effect under polarization potentials of -1.0 to -1.2 V. At a certain polarization potential, the scale inhibition efficiency increases significantly with the increase of PBTCa concentration. The scale inhibition efficiency of 8 mg/L PBTCa reached 98.9% under a polarization potential of -1.0 V. With the negative shift of the cathodic polarization

Table 1

Amount of scale formed on cathode surface (Δm) and the scale inhibition efficiency η_s of PBTCa at different polarization potentials

PBTCa (mg/L)	-1.0 V		-1.1 V		-1.2 V		-1.3 V		-1.4 V		-1.5 V	
	Δm (mg)	η_s (%)	Δm (mg)	η_s (%)	Δm (mg)	η_s (%)	Δm (mg)	η_s (%)	Δm (mg)	η_s (%)	Δm (mg)	η_s (%)
0	9.8	–	16.8	–	17.6	–	19.2	–	20	–	28.4	–
2	5	48.9	15.3	8.9	16.5	6.2	22.3	–	28.5	–	35.4	–
4	4	59.1	8.3	50.5	13	26.1	14.1	26.5	23.7	–	34	–
6	0.9	90.8	2.4	85.7	4.1	76.7	9.9	48.4	19.2	4.0	25.4	10.5
8	0.1	98.9	0.1	99.4	3.3	81.2	7.9	58.8	12.1	39.5	13.6	52.1

potential, the scale inhibition efficiency of PBTCa at the same concentration decreases. When the cathodic polarization potential was shifted to -1.3 V or below, PBTCa at a concentration no more than 4 mg/L not only had no scale inhibition effect but caused more scale to form on the cathode surface in the scaling solution than in the blank. In other words, the scale inhibitor at lower concentrations promoted scale formation on the cathode surface at more negative cathodic polarization potentials.

3.2. Cyclic voltammetry analysis

Figs. 4 and 5 show the cyclic voltammetric curves of the stainless steel electrode in non-scaling and scaling solutions, respectively. The hydrogen evolution reaction mainly occurs when the cathodic reduction potential was more negative than -1.0 V [24]. The polarization current density increased rapidly with the negative shift of polarization potential, that is, the more negative the cathodic polarization potential, the faster the reaction rate of hydrogen evolution on the cathode surface.

It can be seen from Fig. 4 that the addition of PBTCa in the non-scaling solution had almost no effect on the peak potential and strength, indicating that PBTCa was not involved in the electrode reactions. PBTCa hardly affected the rate of hydrogen evolution reaction in the non-scaling

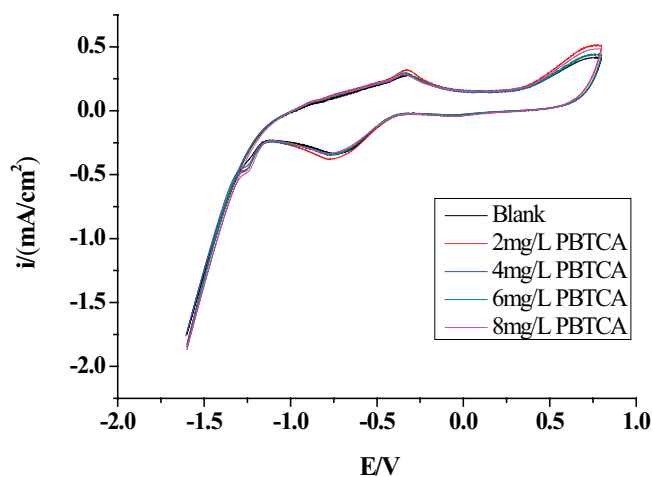


Fig. 4. Cyclic voltammetric curves of stainless steel electrode in non-scaling solution containing PBTCa at different concentrations.

solution when the polarization potential was more negative than -1.0 V. Fig. 5 shows that the polarization current density of the hydrogen evolution reaction was large in the scaling solution without the scale inhibitor, but the addition of PBTCa caused the polarization current density of hydrogen evolution to decrease significantly. The higher the concentration of PBTCa, the smaller the polarization current density of the hydrogen evolution reaction.

3.3. Analysis of solution near cathode surface

Fig. 6 displays the change of Ca^{2+} concentration with PBTCa content in the scaling solution near the cathode surface after cathode polarization at -1.5 V for 1 h. It could be seen that the presence of 2 mg/L PBTCa in the solution could rapidly increase the Ca^{2+} concentration. With the further increase of PBTCa content, the Ca^{2+} concentration in the solution near the cathode surface increased gradually.

PBTCa is a commonly used organic phosphonate scale inhibitor. In aqueous solutions, the PBTCa^{2-} ions can chelate with Ca^{2+} to increase the solubility of scaling ions [27]. The higher the concentration of PBTCa, the more Ca^{2+} is chelated, and the larger the measured Ca^{2+} concentration in the solution.

Fig. 7 shows the change in pH of solution near the cathode surface after cathode polarization at -1.5 V for 1 h in

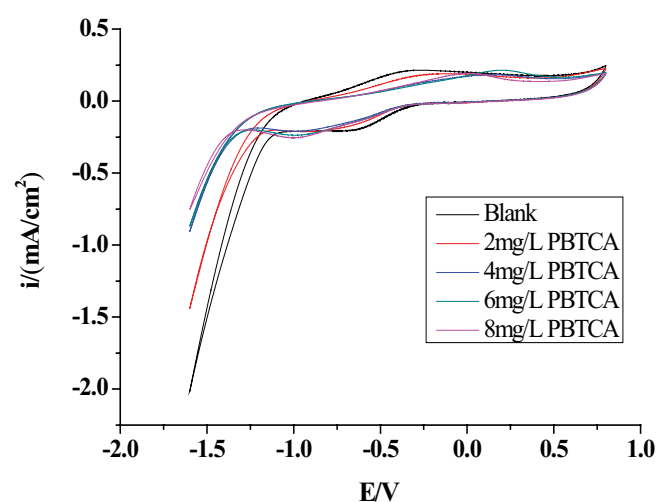


Fig. 5. Cyclic voltammetric curves of stainless steel electrode in scaling solution containing PBTCa at different concentrations.

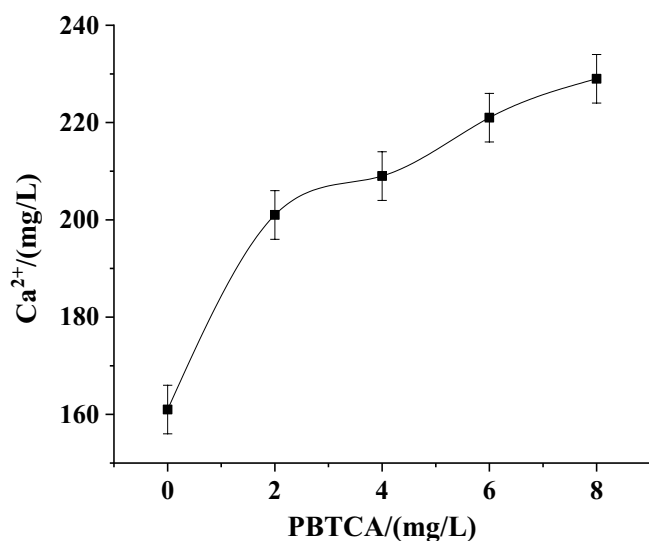


Fig. 6. Change of Ca^{2+} concentration in the scaling solution near the cathode surface with PBTCa concentration after cathodic polarization at -1.5 V for 1 h.

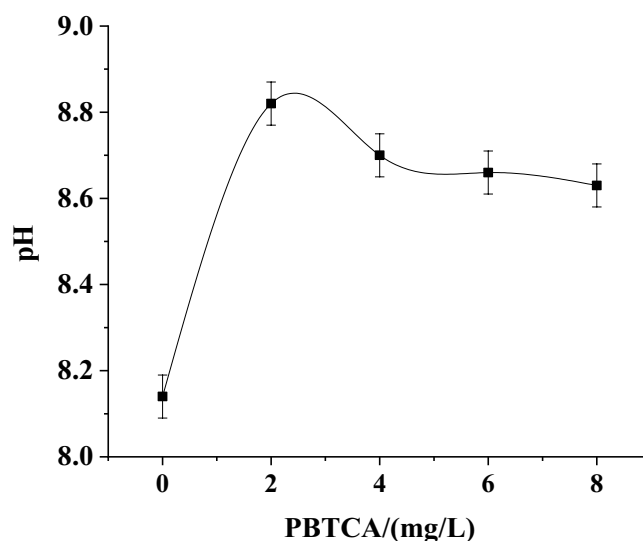


Fig. 7. Change in pH of solution near the cathode surface after cathode polarization at -1.5 V for 1 h in different concentrations of PBTCa.

different concentrations of PBTCa. The results show that the pH of the scaling solution near the cathode surface with no PBTCa is 8.14. The pH values of the solution near the cathode surface containing 2, 4, 6, and 8 mg/L PBTCa are 8.82, 8.70, 8.66, and 8.63, respectively. The pH of the scaling solution near the cathode surface with no PBTCa is significantly lower than that of the solution containing various concentrations of PBTCa. The pH of the solution near the cathode containing 2 mg/L PBTCa is the highest.

Generally, compared with the blank solution, the presence of the scale inhibitor will increase the pH value of the scaling solution [30]. In solutions containing PBTCa, the following reactions would occur:



PBTCa complexes with Ca^{2+} in solution through reaction (5), so that Ca^{2+} could be stabilized in solution and its solubility increased. Hence, reaction (4) was suppressed and part of the HCO_3^- in the solution would undergo CO_2 release reaction through reaction (6) [31], which increased the pH of the solution.

A comparison of cyclic voltammetry curves of the stainless steel electrode in blank solutions is displayed in Figs. 4 and 5. It can be found that the hydrogen evolution rate was higher in the scaling solution than that in the non-scaling solution. This might be due to the occurrence of scaling reaction (4) in the scaling solution, which consumed OH^- and promoted hydrolysis reaction (2) and produced more H^+ , which accelerated the rate of hydrogen evolution reaction (3). In the scaling solution containing PBTCa, the reaction rate of hydrogen evolution on the electrode surface decreased obviously, as shown in Fig. 5. The higher the PBTCa concentration, the lower the reaction

rate of hydrogen evolution. This might be because the occurrence of the complexation reaction (5) inhibited the scaling reaction (4), promoted the CO_2 release reaction (6), raised the pH and decreased the H^+ concentration of the solution and lowered the rate of hydrogen evolution reaction (3).

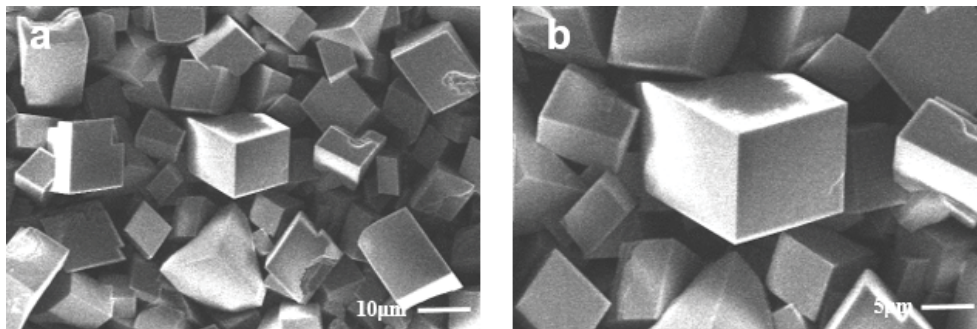
Fig. 7 shows that in the scaling solution containing 2 mg/L PBTCa, the pH of the solution near the cathode surface was the highest after polarization at -1.5 V for 1 h. Compared with the results in solution containing a larger concentration of PBTCa, the hydrogen evolution reaction rate on the cathode surface was significantly higher in solution containing 2 mg/L PBTCa, which made the solution have a higher pH value. Compared with the results in the blank solution, the inhibition of reaction (4) by PBTCa and the occurrence of CO_2 release reaction (6) in the solution containing 2 mg/L PBTCa raised the pH of the solution near the cathode surface and also decreased the rate of hydrogen evolution on the cathode surface.

In addition, the solubility S of CaCO_3 could be calculated by the following formula [32,33]:

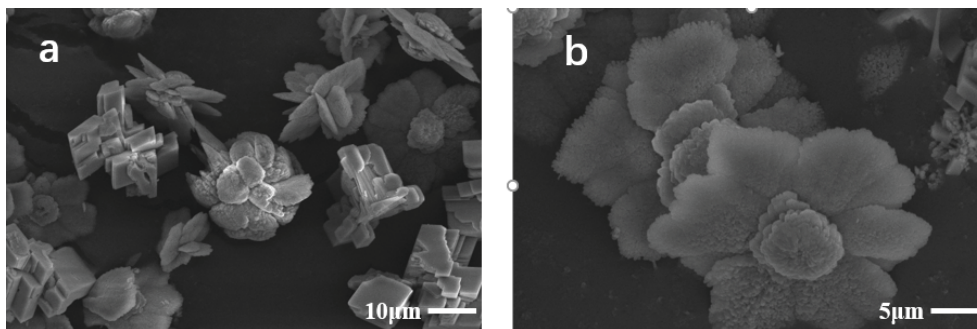
$$S = \left(\frac{K_{\text{sp}} \times 10^{-2\text{pH}} + K_1 \times 10^{-2\text{pH}} + K_1 K_2}{K_1 K_2} \right)^{0.5} \quad (7)$$

where K_1 and K_2 are the acid dissociation constants of H_2CO_3 and HCO_3^- , respectively, and K_{sp} is the solubility product constant of CaCO_3 . Eq. (7) shows that S is a function of pH at constant temperature. In the scaling solution containing different concentrations of PBTCa, according to the change of pH value of the solution near the cathode surface displayed in Fig. 7, the pH in the solution containing 2 mg/L PBTCa is the highest, so the solubility S of CaCO_3 in this solution is the minimum.

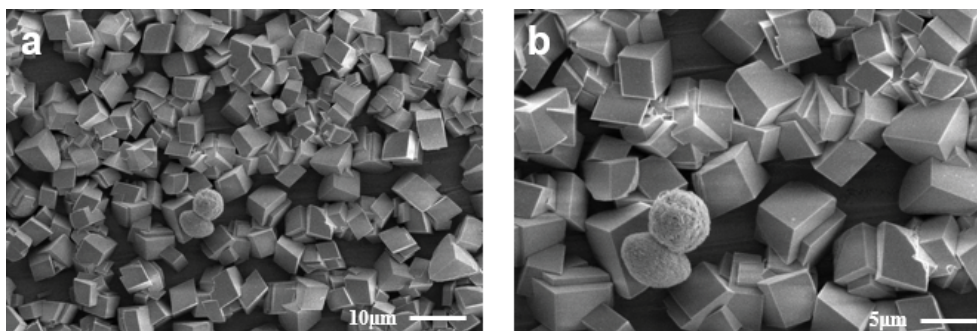
Therefore, in the case of the solution containing 2 mg/L PBTCa under a polarization potential of -1.5 V, the reasons



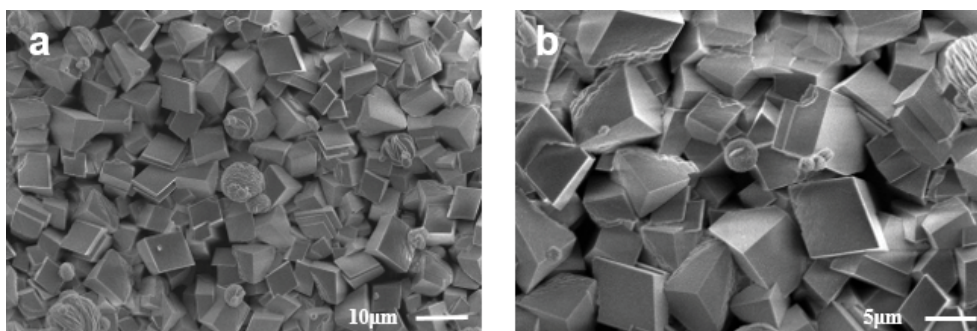
(I)



(II)

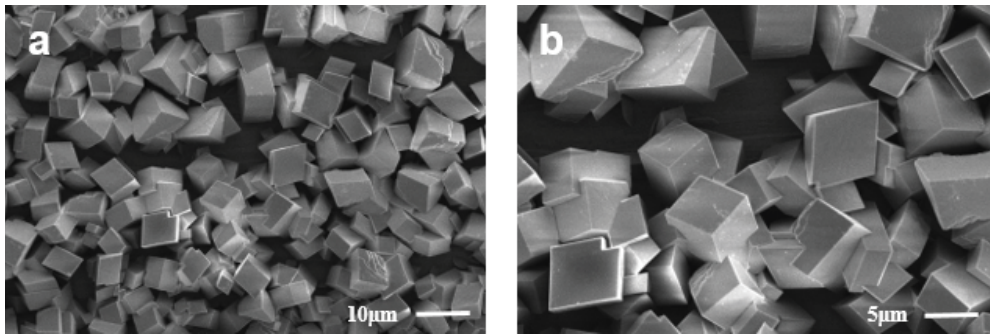


(III)

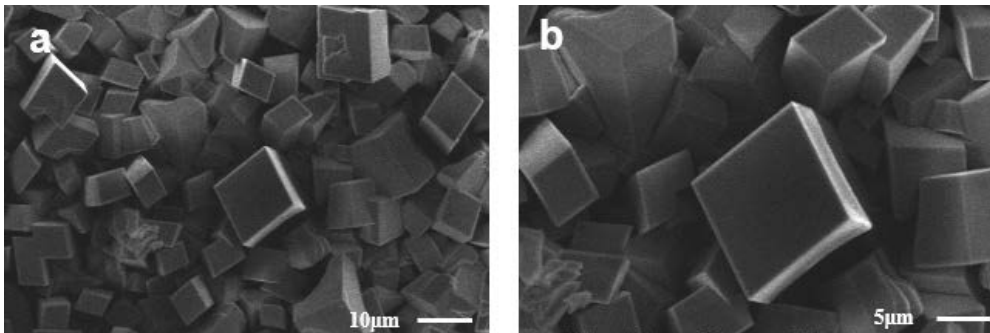


(IV)

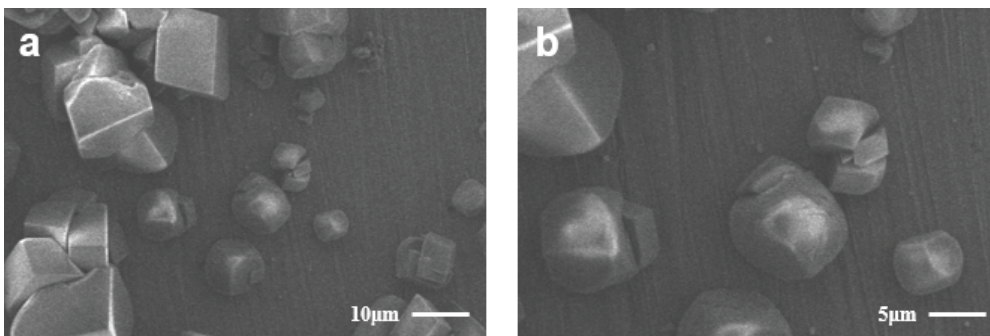
Fig. 8. SEM images of CaCO₃ crystals: (I) in the blank without polarization, (II) containing 2 mg/L of PBTCa without polarization, (III) in the blank under polarization at -1.0 V, and (IV) in the blank under polarization at -1.5 V.



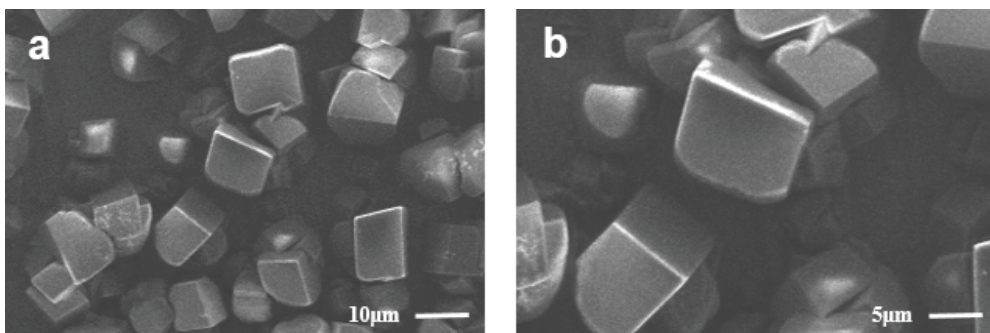
(V)



(VI)



(VII)



(VIII)

Fig. 8. SEM images of CaCO₃ crystals: (V) containing 2 mg/L of PBTCa under polarization at -1.0 V, (VI) containing 2 mg/L of PBTCa under polarization at -1.5 V, (VII) containing 8 mg/L of PBTCa under polarization at -1.0 V, and (VIII) containing 8 mg/L of PBTCa under polarization at -1.5 V.

why the addition of PBTCa promoted scaling on the cathode surface are mainly as follows. First, the solubilization of Ca^{2+} by a lower concentration of PBTCa is limited. Second, the pH of the solution near the cathode surface was the highest and the S value of CaCO_3 was the smallest in this case, so that promoting scaling reaction (4) to deposit more CaCO_3 on the cathode surface. The same results were obtained in a solution containing 4 mg/L PBTCa under a higher polarization potential. However, PBTCa at higher concentrations has scale inhibition performance, which is due to the good solubilization of Ca^{2+} and the occurrence of CO_2 release reaction (6) to inhibit the increase in pH of the scaling solution containing a higher concentration of PBTCa.

3.4. Analysis of morphology and structure of calcium carbonate scale

In a conventional system without polarization, the scale inhibition mechanism of most scale inhibitors (such as PBTCa) can not only increase the solubility of scale-forming ions, but also cause lattice distortion of crystals (such as calcium carbonate). Crystallization of CaCO_3 is a dynamic process involving three stages: nucleation, crystal growth, and phase transformation [34]. In order to explore whether the addition of PBTCa would have an impact on the morphology and structure of the CaCO_3 crystal on the cathode surface during electrolysis, the scale samples on the cathode surface were obtained under different conditions were characterized.

Fig. 8 shows the SEM photographs of CaCO_3 crystals obtained under different conditions. Figs. 8I and II show the crystal morphology of CaCO_3 crystals formed without polarization in the blank and scaling solutions containing PBTCa, respectively. The results show that the CaCO_3 crystals formed in the blank solution have a regular hexahedral structure with a smooth surface and sharp edges, typical of calcite crystals. Calcite is the thermodynamically most stable calcium carbonate crystal with four major growth surfaces (104), (102), (113), and (202) [35,36]. In the scaling solution containing PBTCa, most of the CaCO_3 crystals were converted into a spherical- or petal-like morphology and should be vaterite, which was not easy to accumulate on the solid surface and this is one of the reasons for scale inhibition.

The morphology of scale obtained under cathodic polarization was also observed by SEM. Figs. 8III and IV show photographs of the CaCO_3 samples obtained in the blank scaling solution under polarization at -1.0 and -1.5 V, respectively. The results show that the crystal forms of the CaCO_3 scale samples were mostly typical calcite crystals. A small amount of vaterite with a rough surface was also found on the scale. By comparing the CaCO_3 crystals obtained in the blank solution under different polarization potentials, it can be found that the crystals formed on the cathode surface are more compact under -1.5 V.

Figs. 8V and VI show photographs of the CaCO_3 samples obtained in the scaling solution containing 2 mg/L PBTCa. The scales only showed the morphology of calcite and no other crystalline forms such as vaterite were found. The particle size of calcite increased significantly when the polarization potential drops to -1.5 V. When the

concentration of PBTCa increased to 8 mg/L, the amount of CaCO_3 scales on the cathode surface decreased obviously, especially under the potential of -1.0 V, as shown in Figs. 8VII and VIII. The CaCO_3 samples also appeared in the form of calcite under the two polarization potentials but forming an irregular rhombohedron. The results of Fig. 8 show that PBTCa no longer has the effect of changing the crystal form of calcium carbonate under cathodic polarization. Only a calcite scale was formed on the cathode surface in the scaling solution containing PBTCa under cathodic polarization condition. Despite this, the addition of PBTCa with a high concentration can significantly reduce the amount of scale formed on the cathode surface and showing good scale inhibition performance.

The CaCO_3 crystals were also analyzed by FTIR spectroscopy and the results are shown in Fig. 9. Figs. 9a and b show the FTIR spectra of CaCO_3 samples obtained in the blank and scaling solutions containing 2 mg/L of PBTCa with no polarization, respectively. The absorption peaks of calcite appeared at 713 and 873 cm^{-1} [37] in the blank scale solution. In the scaling solution containing 2 mg/L of PBTCa, in addition to the absorption peaks of calcite at 713 and 873 cm^{-1} , the absorption peak of vaterite also appeared at 1,082 and 745 cm^{-1} .

Figs. 9c and d present the FTIR spectra of CaCO_3 samples obtained in the blank scaling solution under polarization potentials of -1.0 and -1.5 V, respectively, mainly displaying the absorption peaks of calcite located at 713 and 875 cm^{-1} , and the weaker absorption peaks of vaterite located at 1,082 and 745 cm^{-1} . The appearance of a small amount of vaterite on the cathode surface in the blank scaling solution might be due to the action of the electric field.

Figs. 9e and f show the FTIR spectra of CaCO_3 samples obtained in the scaling solution containing 2 mg/L of PBTCa under polarization potentials of -1.0 and -1.5 V. Only the absorption peaks of calcite were observed at 713 and 875 cm^{-1} while the absorption peaks at 1,082 and 745 cm^{-1} related to vaterite disappeared. The FTIR spectra of the CaCO_3 samples obtained in the scaling solution containing 8 mg/L of PBTCa (displayed in Figs. 9g and h) illustrate the same changes as that obtained in the solution containing 2 mg/L of PBTCa. The results are consistent with the results of the SEM images in Fig. 8. It can be concluded that PBTCa can promote the formation of calcite-type CaCO_3 under the conditions of cathodic polarization and even transform some vaterite into calcite. It may also be one of the reasons why the amount of CaCO_3 scale formed on the cathode surface in scaling solution containing 2 mg/L of PBTCa was larger than that in blank scaling solution at a more negative polarization potential.

Figs. 10a and b shows the XRD pattern of the CaCO_3 crystals formed under different conditions. Under the non-polarization conditions, for the CaCO_3 samples formed in the blank solution, the characteristic diffraction peaks of calcite appear at 29.04°, 35.84°, 39.18°, 43.04°, 47.28°, 48.30°, 56.46°, and 57.14°, corresponding to the (104), (110), (113), (202), (018), (116), (211), and (311) crystal planes, respectively. For the CaCO_3 samples formed in the scaling solution containing PBTCa, the characteristic peaks of the vaterite appear at 24.82°, 27.05°, 32.78°, and 50.08°, corresponding to the crystal planes (110), (112), (114), and (118), respectively [38]. Under

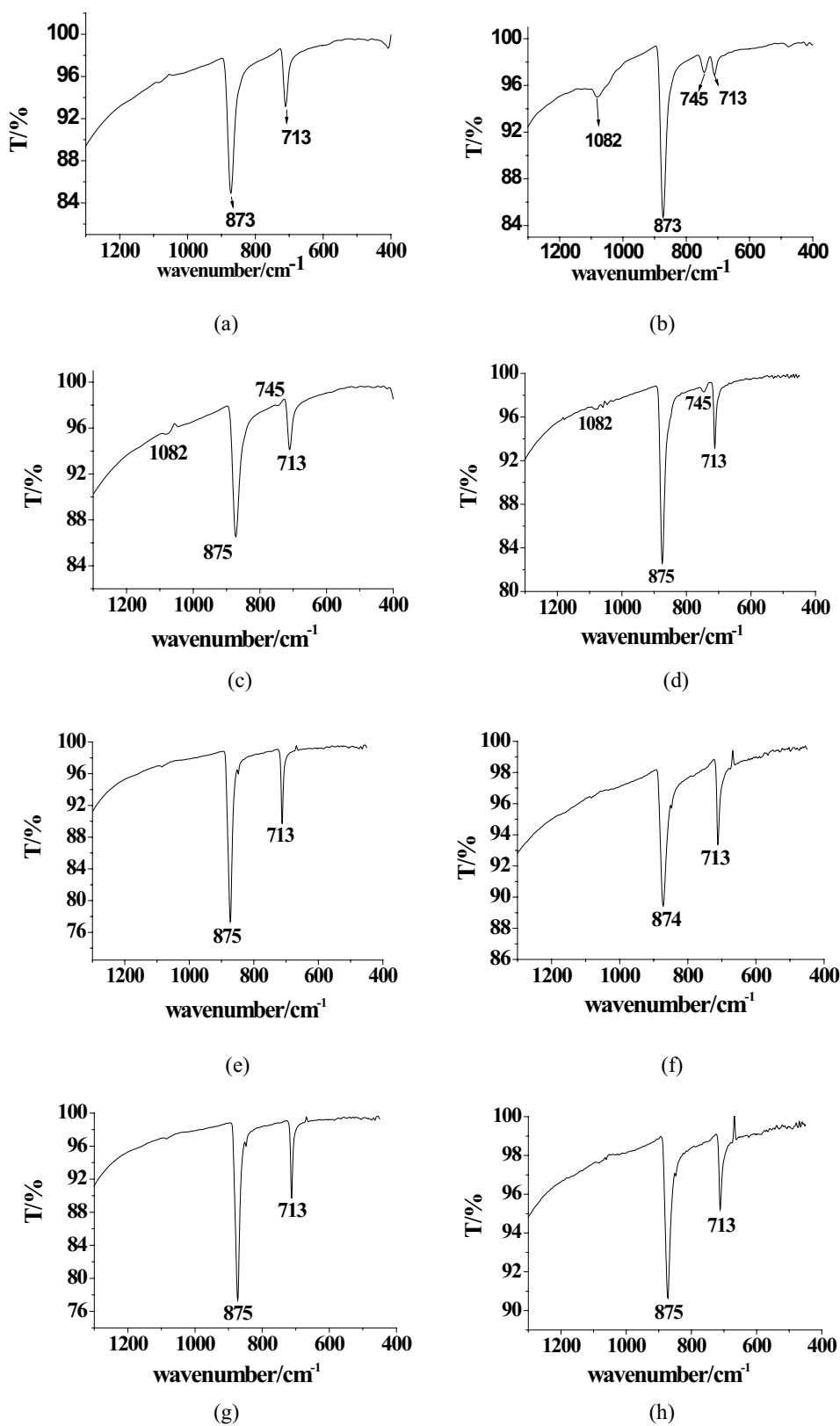


Fig. 9. FTIR spectra of CaCO_3 crystals: (a) in the blank without polarization, (b) containing 2 mg/L of PBTCa without polarization, (c) in the blank under polarization at -1.0 V, (d) in the blank under polarization at -1.5 V, (e) containing 2 mg/L of PBTCa under polarization at -1.0 V, (f) containing 2 mg/L of PBTCa under polarization at -1.5 V, (g) containing 8 mg/L of PBTCa under polarization at -1.0 V, and (h) containing 8 mg/L of PBTCa under polarization at -1.5 V.

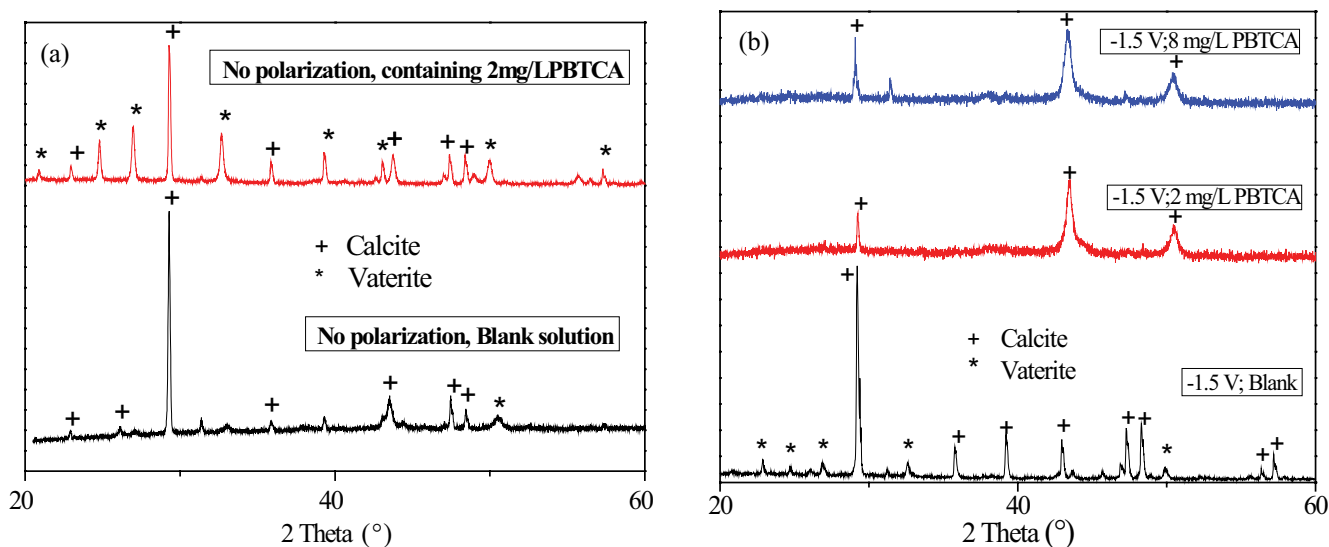


Fig. 10. XRD patterns of CaCO_3 samples (a) without polarization and (b) under cathodic polarization.

polarization conditions, for the CaCO_3 samples formed in the blank solution without PBTCA, the characteristic diffraction peaks of calcite mainly appear with also some weak peaks of vaterite. However, for the CaCO_3 samples formed in the scaling solution containing PBTCA, all the characteristic peaks of vaterite disappear and only the peaks of calcite are found.

3.5. Scale inhibition behavior of PBTCA under cathodic polarization

The crystallization of CaCO_3 begins with the combination of Ca^{2+} and CO_3^{2-} to form crystal embryos. When these crystal embryos reach a critical size, the CaCO_3 can form vaterite, aragonite, or calcite crystals based on the solution conditions [39]. According to the mechanism of dissolution and recrystallization, the formation of the CaCO_3 scale could be divided into three stages: the appearance and disappearance of amorphous CaCO_3 , the appearance and disappearance of metastable vaterite or aragonite, and the development of stable calcite [40]. In some cases, amorphous calcium carbonate can also be directly and rapidly converted into calcite. In general, calcite is the stable phase and final form of calcium carbonate.

In the blank system under cathodic polarization conditions, the presence of a small amount of vaterite on the cathode surface (Figs. 8III and IV) indicates that the cathodic polarization delays the conversion of vaterite to calcite, which may be related to the existence of an electric field.

In general, the scale inhibition effect of PBTCA on calcium carbonate in aqueous solutions is mainly based on the solubilization effect and lattice distortion phenomenon. PBTCA contains phosphonic acid ($-\text{PO}_3\text{H}_2$) and carboxylic acid ($-\text{COOH}$) groups, which are present in the form of ions in neutral and weakly alkaline solutions, whereas $-\text{PO}_3\text{H}-$ and $-\text{COO}-$ can chelate with Ca^{2+} to achieve the solubilization effect of the scaling ions [28]. The lattice distortion of calcium carbonate by PBTCA is mainly due to the adsorption of phosphonic acid groups ($-\text{PO}_3\text{H}_2$) and carboxylic acid groups ($-\text{COOH}$) in PBTCA on the surface of vaterite

crystals, occupying the active site of crystal growth, changing the stereochemical orientation of CaCO_3 growth, thereby inhibiting the transformation of vaterite to calcite [41–43]. From a thermodynamic point of view, the metastable vaterite crystals have a high free enthalpy (which is the sum of the product of surface energy and all the exposed surface areas) and are unstable during the crystallization process [44]. The adsorption of a scale inhibitor can reduce the surface energy and minimize the free enthalpy of the crystals. Thereby, the metastable vaterite can be stably present in solution. Therefore, the key factor in the lattice distortion of the calcium carbonate crystal by the scale inhibitor is its adsorption on the crystal surface.

In the electrochemical system, the scale inhibition effect of PBTCA on calcium carbonate is mainly based on the solubilization effect and no lattice distortion of CaCO_3 crystal would occur. The deposition of CaCO_3 on the cathode surface is easier due to the existence of the hydrogen evolution reaction. Under the action of an electric field, since the PBTCA anion is more likely to face and move to the anode direction, it is difficult for the PBTCA anion to adsorb on the active site of the CaCO_3 crystal on the cathode surface. Therefore, the lattice distortion of the calcium carbonate by PBTCA is not easy to occur under cathodic polarization. Furthermore, the addition of PBTCA leads to an increase in the Ca^{2+} concentration and raise of pH in the solution near the cathode surface, which increases the probability of nucleation and the number of calcium carbonate crystals, accelerates the rate of crystallization, and shortens the nucleation induction period and increases the conversion rate of metastable vaterite to stable calcite. Therefore, in the scaling solution containing low concentrations of PBTCA under a more negative cathodic polarization, the cathode surface is more susceptible to scaling.

4. Conclusion

At cathodic polarization potentials of -1.0 to -1.5 V, scaling occurred on the cathode surface in all the scaling solution,

and the amount of scale increased with the negative shift of the polarization potential. PBTCa showed good scale inhibition performance on the cathode surface and the scale inhibition efficiency increased with the concentration of PBTCa but decreased with the negative shift of the cathode potential. However, a lower concentration of PBTCa promoted scaling on the cathode surface under a more negative cathodic polarization potential, which was related to the increase in the Ca^{2+} concentration and the raise of pH in the solution near the cathode surface by PBTCa. In addition, most of the CaCO_3 crystals formed on the cathode surface were calcite, as well as a small amount of vaterite in the blank scaling solution. In the scaling solutions containing PBTCa, all the formed CaCO_3 crystals were calcite. PBTCa did not exhibit the lattice distortion effect on calcium carbonate crystals and the scale inhibition of PBTCa on calcium carbonate is mainly due to its solubilization effect on calcium ions.

Acknowledgments

The authors acknowledge the financial support of the National Natural Science Foundation of China (51471104) and Science and Technology Commission of Shanghai Municipality (17DZ2282800).

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