Formation and Inhibition of Calcium Carbonate Crystals under Cathodic Polarization Conditions

Kun Sheng, Honghua Ge *, Xin Huang, Yi Zhang, Yanfang Song, Fang Ge, Yuzeng Zhao and Xinjing Meng

Shanghai Engineering Research Center of Energy-Saving in Heat Exchange Systems, Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai University of Electric Power, Shanghai 200090, China; kunsheng2916@163.com (K.S.); hxqiuren@163.com (X.H.); zzyyyy1997@163.com (Y.Z.); yanfang_song16@163.com (Y.S.); ShainSQian@outlook.com (F.G.); zhaoyuzeng@shiep.edu.cn (Y.Z.); mengxinjing@shiep.edu.cn (X.M)
* Correspondence: gehonghua@shiep.edu.cn; Tel./Fax: +86-21-6041-4107

Received: 19 February 2020; Accepted: 4 April 2020; Published: 6 April 2020

Abstract: The formation of CaCO\textsubscript{3} crystals on the cathode surface and the scale-inhibition performance of scale inhibitor 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) on the cathode surface were studied by methods of solution analysis, gravimetric analysis, SEM, FTIR, and XRD techniques. They were then compared with the results of the formation and suppression of CaCO\textsubscript{3} crystals in aqueous solution. PBTCA had a good solution-scale-inhibition performance and good lattice-distortion effects on CaCO\textsubscript{3} crystals in solution, which could change the CaCO\textsubscript{3} from calcite to vaterite and aragonite crystals. The solution-scale-inhibition efficiency exceeded 97% when the PBTCA concentration reached 8 mg/L. Under cathodic polarization conditions, the surface-scale-inhibition efficiency of the cathode and solution-scale-inhibition efficiency near the cathode surface both exceed 97% at polarization potential of −1V. The addition of PBTCA significantly reduced the amount of CaCO\textsubscript{3} crystals formed on the cathode surface and had good surface and solution-scale-inhibition effect. However, the lattice-distortion effect of PBTCA on CaCO\textsubscript{3} crystals disappeared on the cathode surface, and the resulting CaCO\textsubscript{3} contained only calcite crystals. The high-scale-inhibition effect of PBTCA under cathodic polarization was mainly due to the inhibition of the formation of calcium carbonate crystals by PBTCA, and not because of the lattice distortion of CaCO\textsubscript{3} crystals.

Keywords: calcium carbonate crystals; cathodic polarization; crystal distortion; cathode scale inhibition; 2-phosphonobutane-1,2,4-tricarboxylic acid

1. Introduction

The scaling phenomenon is common in industrial production processes, such as circulating cooling water systems, oil field facilities, and pipe flow systems [1–3]. In most cases, the scale-forming substances are apt to appear on heat-exchange surfaces. As the solubility of most scale-forming substances such as CaCO\textsubscript{3} decreases with increasing temperature, it is easy for scale-forming substances to form on heat exchange surfaces which have higher temperatures [4]. However, there are exceptions. For examples, when a piece of electrocatalytic oxidation equipment is used to degrade organic pollutants, such as printing and dyeing wastewater, petroleum, and chemical wastewater [5,6], the pH value of solution near the cathode surface would increase due to the hydrogen evolution reaction at the cathode [7], causing the precipitation of insoluble substances, such as calcium salt, on the surface of the cathode. The nature of scaling is usually the precipitation, adhesion, and film formation of inorganic salt crystals on the solid surfaces. The scaling on the heat-exchange surfaces causes a decrease in heat-exchange efficiency and an increase in the energy consumption of the system [8,9]. Scaling on the cathode...
surface of an electrocatalytic oxidation device would reduce the output current of the device, greatly reducing the degradation efficiency to organic pollutants, until the device cannot operate normally. The deposition of these scaling substances on metal surfaces can also cause problems, such as local overheating and under-scale corrosion [10], which shortens the service life of the equipment.

There are relatively mature techniques for controlling the scaling on heat-exchange surfaces, such as cooling water pipes [11]. The commonly used scaling-control methods can be divided into chemical and physical methods, including the use of scale inhibitor, dilute acid, ion-exchange resin, ultrasonic descaling device, magnetization treatment, membrane treatment, electrostatic water treatment, and so on [12–15]. Chemical scale inhibitors are the most widely used scale-inhibition method in industrial production. A series of scale inhibitors have been developed [16–18]. PBTCA (2-phosphonobutane-1,2,4-tricarboxylic acid) is currently widely used as a scale and corrosion inhibitor because of its low phosphorus content and good scale- and corrosion-inhibition performance [19–21]. However, there are few reports on the formation and control of scaling substances on the surface of cathodes in equipment such as electrocatalytic oxidation. Tang et al. [22] established an evaluation method of scale-inhibition performance by electrochemical means. They used electrochemical method to promote scale formation and evaluate scale-inhibition performance by means of weighing. However, there was almost no analysis of morphology and crystal-form changes of scale generated by electrochemistry.

In this paper, the formation of CaCO$_3$ crystals on the cathode surface under the condition of cathodic polarization was studied, as well as the scale-inhibition effect of the commonly used scale inhibitor PBTCA on the cathode surface. The results were compared with the formation and suppression trend of calcium carbonate crystals in the traditional aqueous solutions. It is hoped to provide a reference for scaling control on the surface of cathodes in equipment such as electrocatalytic oxidation.

2. Materials and Methods

2.1. Experimental Medium

PBTCA was provided by the Shanghai Duojia Water Treatment Company in China. Reagents such as CaCl$_2$, NaHCO$_3$, and disodium edetate (EDTA) for titration were purchased from Sinopharm chemical Reagent Co., Ltd., in China, and the chemicals used were analytical grade. All test solutions were prepared with deionized water.

2.2. Solution-Scale-Inhibition Experiments

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 (named “determination of scale-inhibition performance of water treatment agents—Calcium carbonate precipitation method”). The initial pH of the solution was kept at 9.0 by using borax buffer. Scale-formation experiments were carried out in a water bath, at 50 °C for 10 h, and then the scaling solutions were filtered, and the calcium ion concentrations in the filtrate were determined by titration of disodium edetate (EDTA) standard solution. According to the change in calcium ion concentration in the solution before and after the experiments, the solution-scale-inhibition efficiency, $\eta_s$, was calculated according to the following formula:

$$\eta_s = \frac{c_2 - c_1}{c_0 - c_1} \times 100\%$$

(1)

where $c_0$ is the concentration of calcium ions in the scaling solution before the experiment (mol/L), $c_1$ is the concentration of calcium ions in the blank scaling solution after the experiment (mol/L), and $c_2$ is the concentration of calcium ions in the scaling solution containing PBTCA after the experiment (mol/L).
2.3. Scale-Inhibition Experiments under the Cathodic Polarization

The cathodic polarization was performed on a potentiostat. 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 was a saturated calomel electrode (SCE). The stainless steel was sanded with 500 to 1500 mesh sandpapers, wiped with alcohol, and washed with deionized water before each test.

The scale-forming experiments were carried out on a stainless-steel cathode by applying different polarization potentials (−1.0 and −1.5 V) for 1 h. The scaling solution was the same as that in Section 2.2. The stainless-steel cathode was weighed before and after the experiment, with weight increase after the experiment being the amount of scale formed on the stainless-steel surface (the weight of the stainless-steel cathode itself did not change during the experiment). The surface-scale-inhibition efficiency \( \eta_w \) was calculated as follows:

\[
\eta_w = \frac{\Delta m_1 - \Delta m_2}{\Delta m_1} \times 100\%
\]

where \( \Delta m_1 \) is the weight increase of the stainless-steel cathode after the experiment in the scaling solution with no additives, and \( \Delta m_2 \) is the weight increase of the stainless-steel cathode after the experiment in the scaling solution with the scale inhibitor.

2.4. Morphology and Structure Analysis of CaCO₃ Crystals

The CaCO₃ crystals were dried and sprayed with Au, and the surface morphology was observed by a scanning electron microscopy (SEM) (JSM-7800F), under an acceleration voltage of 15 kV. The crystal structure and type of the CaCO₃ crystals was analyzed by Fourier transform infrared (FTIR) spectroscopy (Spectrum Two) (FTIR-8400 S, Shimadzu Co. Ltd., Japan), in the range of 400 to 2000 cm\(^{-1}\), and the X-ray diffraction (XRD) was recorded on (D8 ADVANCE, Germany)(Cu, K\(\alpha\); the diffraction angle (2\(\theta\)) in the range of 20°–80° was scanned.

3. Results and Discussion

3.1. Formation and Inhibition of CaCO₃ Crystals in Solution

First, the scale inhibition performance of PBTCA in the scaling solution was measured. The results of the solution-scale-inhibition efficiency, \( \eta_s \), of the scale inhibitor PBTCA with different concentrations are shown in Table 1. PBTCA is an organic phosphine carboxylic acid scale inhibitor and is commonly used in cooling water systems. Table 1 shows that the scale-inhibition efficiency, \( \eta_s \), increased as the raise of PBTCA concentration. When the PBTCA concentration reached 4 mg/L, the \( \eta_s \) value reached 96%. The value of \( \eta_s \) changed little when the PBTCA concentration continued to increase. Many scale inhibitors, including PBTCA can adsorb and chelate with calcium ions, reducing the supersaturation of the scaling solution and thus reducing the nucleation rate of CaCO₃ crystals, therefore inhibiting the deposition of CaCO₃ \([23,24]\). During the nucleation of the crystal, the scale inhibitor might also form slightly soluble calcium salts with calcium ions and encapsulate the surface of solid impurities which act as a crystal center, thereby preventing the nucleation and growth of CaCO₃ crystals on the solid impurities \([25]\). During the growth period of the crystal, the scale inhibitor can be adsorbed on the active site of the surface of the calcium carbonate crystal, inhibit, and delay the crystallization and growth of calcium carbonate \([26,27]\).

| Concentration of PBTCA (mg/L) | 2      | 4      | 8      |
|-------------------------------|--------|--------|--------|
| \( \eta_s \) (%)             | 75 ± 2 | 96 ± 3 | 97 ± 3 |
CaCO$_3$ crystals formed in the scaling solution or heat-exchange surface that do not use any scale-inhibition technique exhibit a sharp-edged cube structure, as shown in Figure 1(1). These crystals have smooth surfaces and exhibit regular calcite morphology. The chemical scale inhibitor PBTCA was added for scale control. Figure 1(2) shows the morphology of CaCO$_3$ crystals formed in the scaling solution containing 8 mg/L PBTCA. It can be found that most of CaCO$_3$ crystals have been transformed into spherical vaterite or petal-shaped aragonite. Among the crystal forms of calcium carbonate, calcite is the thermodynamically most stable CaCO$_3$ crystal with four major growth surfaces of (104), (102), (113), and (202) [28,29]. Compared with calcite, vaterite or aragonite is less likely to adhere on solid surfaces, which is one of the reasons why scale inhibitors play a role in preventing scaling.

![Figure 1](image1.jpg)

**Figure 1.** SEM images of CaCO$_3$ crystals generated in scale solution: (1) blank; (2) containing 8 mg/L PBTCA.

FTIR spectra can be used to further analyze the crystal form of CaCO$_3$ and the effect of scale inhibitor. Figure 2 shows the infrared spectrum of CaCO$_3$ crystals generated in the scaling solution. For CaCO$_3$ crystals formed in the blank scaling solution (Figure 2(1)), only the absorption peaks of calcite appeared at 713 and 873 cm$^{-1}$ [30]. In the scaling solution containing 8 mg/L of PBTCA (Figure 2(2)),
in addition to the absorption peaks of calcite at 713 and 873 cm\(^{-1}\), the absorption peak of vaterite also appeared at 745 cm\(^{-1}\), and a weaker absorption peak of aragonite appeared at 854 cm\(^{-1}\) [31].

Figure 2. FTIR spectra of CaCO\(_3\) crystals in the scaling solution: (1) blank; (2) containing 8 mg/L PBTCA.

Figure 3 shows the XRD pattern of the CaCO\(_3\) crystals formed in the blank scaling solution and in the solution containing 8 mg/L PBTCA. The CaCO\(_3\) crystals formed in the blank scaling solution exhibit only the characteristic diffraction peaks of calcite, as shown in Figure 3(1). In addition to the characteristic diffraction peaks of calcite, the characteristic peaks of vaterite appeared for the CaCO\(_3\) crystals formed in the scaling solution containing PBTCA (as shown in Figure 3(2)).
3.2. Formation and Inhibition of CaCO$_3$ on the Cathode Surface

3.2.1. CaCO$_3$ Crystals Formed on the Cathode Surface

Figure 4 shows photographs of the CaCO$_3$ crystals obtained on the cathode surface in the blank scaling solution under polarization at $-1.0$ and $-1.5$ V, respectively. The results show that the formed CaCO$_3$ were mostly typical calcite crystals. There was also a small amount of vaterite with a rough surface, which might be due to the effect of the electric field under cathodic polarization. Comparing the particle size of CaCO$_3$ crystals attached to the cathode surface at different polarization potentials, it could be found that the particle size of CaCO$_3$ crystals produced on the cathode surface was larger under $-1.5$ V polarization.
Figure 4. The morphology of CaCO$_3$ crystals generated on the cathode surface in the blank scaling solution, under different polarization potentials. (1) Polarization at −1.0 V; (2) Polarization at −1.5 V.

Figure 5 presents the FTIR spectra of CaCO$_3$ crystals obtained on the cathode surface in the blank scaling solution under polarization potentials of −1.0V and −1.5V, respectively. The absorption peaks of calcite located at 713 and 875 cm$^{-1}$ mainly appeared, which were consistent with the results observed by SEM. A weak absorption peak at 745 cm$^{-1}$ corresponding to vaterite was also found, indicating that the application of cathodic polarization had a certain effect on the CaCO$_3$ crystal form.
Figure 5. FTIR spectra of CaCO$_3$ crystals on the cathode surface in the blank scaling solution, under different polarization potentials. (1) Polarization at $-1.0$ V; (2) Polarization at $-1.5$ V.

3.2.2. Scale Inhibition of PBTCA on the Formation of CaCO$_3$ on the Cathode Surface

The cathode surface-scale-inhibition efficiency ($\eta_w$) and the solution-scale-inhibition efficiency ($\eta_s$) near the cathode surface of PBTCA at various concentrations under different polarization potentials are shown in Table 2. Compared with the blank solution, the addition of PBTCA at all concentrations used in this paper has both solution and cathode surface-scale-inhibition effects, and with the increase of PBTCA concentration, the scale-inhibition efficiency increases significantly. Under a polarization potential of $-1.0$ V, the cathodic-scale-inhibition efficiency and solution-scale -inhibition efficiency of 8 mg/L PBTCA both reached 97%. When the cathodic polarization potential was shifted to $-1.5$ V, the cathodic-scale-inhibition efficiency and solution-scale-inhibition efficiency of 8 mg/L PBTCA has decreased to 72% and 87%, respectively.

Table 2. The cathode surface-scale-inhibition efficiency ($\eta_w$) and the solution-scale-inhibition efficiency near the cathode surface ($\eta_s$) of PBTCA under different polarization potentials.

| Potentials (V) | $\eta_w$ (%) | $\eta_s$ (%) |
|----------------|--------------|--------------|
|                | 2            | 4            | 8            | 2            | 4            | 8            |
| Concentration of PBTCA (mg/L) | 25 ± 1       | 47 ± 2       | 97 ± 3       | 18 ± 1       | 38 ± 2       | 72 ± 3       |
|                | 43 ± 2       | 83 ± 3       | 97 ± 3       | 32 ± 2       | 62 ± 2       | 87 ± 3       |

Figure 6 shows photographs of the CaCO$_3$ crystals obtained on the cathode surface in the scaling solution containing 8 mg/L PBTCA, under polarization at $-1.0$ and $-1.5$ V, respectively. Compared with Figure 4, it can be found that the CaCO$_3$ crystals attached to the cathode surface were significantly reduced. There was less CaCO$_3$ crystals adhesion on the cathode surface, and the crystal size was smaller when polarized at $-1.0$ V than that polarized at $-1.5$ V. In addition, the CaCO$_3$ crystals generated under cathodic polarization gradually began to lose their edges and corners from the original hexagonal structure, but still showed the morphological characteristics of calcite.
Figure 6. The morphology of CaCO$_3$ crystals on the cathode surface in the scaling solution containing 8 mg/L PBTCA, under different polarization potentials. (1) Polarization at $-1.0$ V; (2) Polarization at $-1.5$ V.

In the scaling solution containing 8 mg/L PBTCA, the FTIR spectra of CaCO$_3$ crystals formed on the cathode surface at polarization potentials of $-1.0$ and $-1.5$ V are shown in Figure 7. Only the absorption peaks at 713 and 873 cm$^{-1}$ corresponding to calcite appeared. Compared with Figure 2(2), the characteristic absorption peaks of vaterite and aragonite no longer appear, indicating that, in the case of cathodic polarization, the effect of the scale inhibitor PBTCA on the lattice distortion of CaCO$_3$ disappeared. The addition of PBTCA suppressed the formation of vaterite or aragonite on the cathode surface.
Figure 7. FTIR spectra of CaCO$_3$ crystals on the cathode surface in the scaling solution with 8 mg/L PBTCA, under different polarization potentials. (1) Polarization at $-1.0$ V; (2) Polarization at $-1.5$ V.

Figure 8 shows the XRD pattern of the CaCO$_3$ crystals obtained on the cathode surface under polarization at $-1.5$ V in the blank solution and in solution containing 8 mg/L PBTCA. It was found that, under the condition of cathodic polarization, the CaCO$_3$ crystals formed on the cathode surface in the blank scaling solution mainly exhibited the characteristic diffraction peaks of calcite, as well as a small diffraction peak of vaterite (curve (1) in Figure 8). However, for CaCO$_3$ crystals formed on the cathode surface in the solution containing PBTCA, only diffraction peaks of calcite (curve (2) in Figure 8) appeared. This result was consistent with the results of SEM and FTIR.
3.3. Mechanism Analysis

The crystallization of CaCO$_3$ begins with the combination of Ca$^{2+}$ and CO$_3^{2-}$ to form crystal embryos in the scaling solution. When these crystal embryos reach a critical size, the CaCO$_3$ can form vaterite, aragonite, or calcite crystals, based on the solution conditions [32]. According to the mechanism of dissolution and recrystallization, the formation of the CaCO$_3$ crystals 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 [33].

In general systems such as heat exchange surfaces, there are two main ways for PBTCA to inhibit the formation of CaCO$_3$: complexation effect and lattice distortion of crystals [34]. PBTCA exists in the form of ions in neutral and weakly alkaline solutions. It contains phosphonic acid group (-PO$_3$H$_2$) and carboxylic acid group (-COOH), where -PO$_3$H- and -COO- can adsorb and chelate with Ca$^{2+}$ to inhibit the formation of calcium carbonate crystal [20]. The lattice distortion of CaCO$_3$ by PBTCA is mainly due to the adsorption of the groups -PO$_3$H$_2$ and -COOH in PBTCA on the surface of vaterite crystals, occupying the active sites of crystal growth, changing the stereochemical orientation of CaCO$_3$ growth, thereby inhibiting the transformation of vaterite to calcite [35–37]. From a thermodynamic point of view, the metastable vaterite crystals have a high free enthalpy and are unstable during the crystallization process [26]. 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 a solution containing a scale inhibitor such as PBTCA. The key factor of lattice distortion of the CaCO$_3$ crystals is the adsorption of the scale inhibitor on the crystal surface.

In the electrocatalytic oxidation system, the hydrogen evolution reaction mainly occurs on the cathode surface, which will increase the pH value of the solution near the cathode surface and promote the formation and adhesion of CaCO$_3$ crystals on cathode surface. The following reactions occur on the cathode surface:

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$$  \hspace{1cm} (3)

$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$$  \hspace{1cm} (4)

$$\text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{CaCO}_3 + \text{H}_2\text{O}$$  \hspace{1cm} (5)
With the negative shift of the cathodic polarization potential, the rate of the hydrogen evolution reaction, Equation (2), on the cathode surface increases, which further increases the pH value of the solution near the cathode surface and accelerates the scale formation reaction, Equation (3), resulting in more CaCO\textsubscript{3} crystals with larger particle sizes on the cathode surface (see Figure 4). In addition, under the action of an electric field during cathodic polarization, possibly because the scale inhibitor PBTCA anions are aligned toward the anode, it is difficult for the PBTCA anion to adsorb on the active sites of the CaCO\textsubscript{3} crystals on the cathode surface. Therefore, the lattice distortion of the CaCO\textsubscript{3} crystals by PBTCA is not easy to occur under cathodic polarization. The pH value of the solution near the cathode in the blank scaling solution and the scaling solution containing PBTCA was measured after the cathodic polarization experiments. The pH near the cathode was between 9.0 and 9.5. Under different pH conditions, the types and contents of the complex products of PBTCA and calcium ions are different [38]. In this pH range, the main product of complexation between PBTCA and calcium ions is [Ca(H\textsubscript{3}PBTC)(H\textsubscript{2}O)\textsubscript{2}·2H\textsubscript{2}O]\textsubscript{n}, with a stability constant of 7.55 [39], which is relatively stable in solution. Therefore, under cathodic polarization conditions, the scale-inhibition effect of PBTCA was achieved by preventing the formation of calcium carbonate crystals on the cathode surface, rather than by lattice distortion of CaCO\textsubscript{3} crystals. The scale-inhibition efficiency of the scale inhibitors under cathodic polarization was almost independent of the crystal-distortion effect of CaCO\textsubscript{3} crystals, which is similar to the results of Popov et al. [40].

4. Conclusions

PBTCA had strong solution-scale-inhibition and lattice-distortion effects on the CaCO\textsubscript{3} crystals generated in the scaling solution. When the PBTCA concentration reached 8 mg/L, the solution-scale-inhibition efficiency exceeded 97%, and the solution-scale-inhibition efficiency increases with the increase of PBTCA concentration. The CaCO\textsubscript{3} crystals generated in the blank scaling solution were mostly regular hexagonal. The FTIR and XRD results showed that they were calcite crystals, and the CaCO\textsubscript{3} crystals generated in the scaling solution, containing PBTCA, were spherical and irregular petal-shaped vaterite and aragonite.

In the scaling solution containing PBTCA, the amount of CaCO\textsubscript{3} crystals formed on the cathode surface was greatly reduced, showing good surface scale inhibition of PBTCA. Under a polarization potential of -1.0 V, the cathodic-scale-inhibition efficiency and solution-scale-inhibition efficiency of 8 mg/L PBTCA both reached 97%. The scale-inhibition performance of PBTCA was enhanced with the increase of its concentration and decreased with the negative shift of the polarization potential. Under cathodic polarization conditions, the more negative the polarization potential, the more CaCO\textsubscript{3} crystals generated on the cathode surface and the larger the particle size. Most of the CaCO\textsubscript{3} crystals formed on the cathode surface in the blank scaling solution and the scaling solution containing PBTCA were calcite crystals. PBTCA no longer had a lattice-distortion effect on CaCO\textsubscript{3} crystals on the cathode surface. The scale-inhibition effect of PBTCA under cathodic polarization has no obvious relationship with the crystal-distortion effect caused by PBTCA.

Author Contributions: Conceptualization, H.G.; data curation, K.S.; formal analysis, K.S.; funding acquisition, H.G.; investigation, K.S.; methodology, K.S.; project administration, K.S. and H.G.; resources, H.G.; supervision, H.G.; validation, K.S. and X.H.; writing—original draft, K.S.; writing—review and editing, K.S., H.G., X.H., Y.Z., Y.S., F.G., Y.Z., and X.M. All authors have read and agree to the published version of the manuscript.

Funding: This work is supported by the National Natural Science Foundation of China (Grant No. 51471104), and Science and Technology Commission of Shanghai Municipality (Grant Nos. 18DZ2204500 and 19DZ2271100).

Acknowledgments: The authors acknowledge the financial support of the National Natural Science Foundation of China (No. 51471104) and Science and Technology Commission of Shanghai Municipality (Nos. 18DZ2204500 and 19DZ2271100).

Conflicts of Interest: The authors declare no conflict of interest.
References

1. Zhang, P.; Liu, Y.; Zhang, N.; Ip, W.F.; Kan, A.T.; Tomson, M.B. A novel attach-and-release mineral scale control strategy: Laboratory investigation of retention and release of scale inhibitor on pipe surface. *J. Ind. Eng. Chem.* 2019, 70, 462–471. [CrossRef]

2. Dayaratne, H.N.P.; Jeong, S.; Jang, A. Chemical-free scale inhibition method for seawater reverse osmosis membrane process: Air micro-nano bubbles. *Desalination* 2019, 461, 1–9. [CrossRef]

3. Xu, Y.; Liu, M.; Zhu, J.; Li, H.; Zhou, W. Novel methods of oil fouling inhibition on surface of plate heat exchanger in simulated oilfield geothermal water. *Int. J. Heat Mass Transf.* 2017, 113, 961–974. [CrossRef]

4. Al-Roomi, Y.M.; Hussain, K.F.; Al-Rifaie, M. Performance of inhibitors on CaCO$_3$ scale deposition in stainless steel & copper pipe surface. *Desalination* 2015, 375, 138–148.

5. Song, S.; Fan, J.; He, Z.; Zhan, L.; Liu, Z.; Chen, J.; Xu, X. Electrochemical degradation of azo dye CI Reactive Red 195 by anodic oxidation on Ti/SnO$_2$–Sb/PbO$_2$ electrodes. *Electrochim. Acta.* 2010, 55, 3606–3613. [CrossRef]

6. Fabiánska, A.; Białk-Bielińska, A.; Stepnowski, P.; Stolte, S.; Siedlecka, E.M. Electrochemical degradation of sulfonamides at BDD electrode. *Electrochim. Acta.* 2014, 280, 579–587. [CrossRef]

7. Ketrane, R.; Saidani, B.; Gil, O.; Leleyter, L.; Baraud, F. Efficiency of five scale inhibitors on calcium carbonate precipitation from hard water: Effect of temperature and concentration. *Desalination* 2009, 249, 1397–1404. [CrossRef]

8. Xu, Z.; Zhao, Y.; Wang, J.; Chang, H. Inhibition of calcium carbonate fouling on heat transfer surface using sodium carboxymethyl cellulose. *Appl. Therm. Eng.* 2009, 148, 1074. [CrossRef]

9. Shakkthivel, P.; Vasudevan, T. Acrylic acid-diphenylamine sulphonic acid copolymer threshold inhibitor for sulphate and carbonate scales in cooling water systems. *Desalination* 2006, 197, 179–189. [CrossRef]

10. Zhu, T.; Wang, L.; Sun, W.; Wang, M.; Tian, J.; Yang, Z.; Liu, G. The role of corrosion inhibition in the mitigation of CaCO$_3$ scaling on steel electrode. *Corros. Sci.* 2018, 140, 182–195. [CrossRef]

11. Lourteau, T.; Berrieche, H.; Kécil, K.; Heim, V.; Bricault, D.; Litaudon, M.; Cheap-Charpentier, H. Scale inhibition effect of *Hylocereus undatus* solution on calcium carbonate formation. *J. Cryst. Growth* 2019, 524, 125161. [CrossRef]

12. Chen, Y.; Sun, S.; Lai, Y.; Ma, C. Influence of ultrasound to convectional heat transfer with fouling of cooling water. *Appl. Therm. Eng.* 2016, 100, 340–347. [CrossRef]

13. Xu, Z.; Chang, H.; Wang, B.; Wang, J.; Zhao, Q. Characteristics of calcium carbonate fouling on heat transfer surfaces under the action of electric fields. *J. Mech. Sci. Technol.* 2018, 32, 3445–3451. [CrossRef]

14. Han, Y.; Zhang, C.; Wu, L.; Zhang, Q.; Zhu, L.; Zhao, R. Influence of alternating electromagnetic field and ultrasonic on calcium carbonate crystallization in the presence of magnesium ions. *J. Cryst. Growth* 2018, 499, 67–76. [CrossRef]

15. Xuefèi, M.; Lan, X.; Jiapeng, C.; Zikang, Y.; Wei, H. Experimental study on calcium carbonate precipitation using electromagnetic field treatment. *Water. Sci. Technol.* 2013, 67, 2784–2790. [CrossRef] [PubMed]

16. Belarbi, Z.; Gamby, J.; Makhloufi, L.; Sotta, B.; Tribollet, B. Inhibition of calcium carbonate precipitation by aqueous extract of *Paronychia argentea*. *J. Cryst. Growth* 2014, 386, 208–214. [CrossRef]

17. Huang, H.; Yao, Q.; Jiao, Q.; Liu, B.; Chen, H. Polyepoxysuccinic acid with hyper-branched structure as an environmentally friendly scale inhibitor and its scale inhibition mechanism. *J. Saudi. Chem. Soc.* 2019, 23, 61–74. [CrossRef]

18. Cheap-Charpentier, H.; Gelus, D.; Pécoul, N.; Perrot, H.; Lédion, J.; Horner, O.; Roussi, F. Antiscalant properties of *Spergularia rubra* and *Parietaria officinalis* aqueous solutions. *J. Cryst. Growth* 2016, 443, 43–49. [CrossRef]

19. Xu, Z.B.; Wang, W.L.; Huang, N.; Wu, Q.Y.; Lee, M.Y.; Hu, H.Y. 2-Phosphonobutane-1, 2, 4-tricarboxylic acid (PBTCA) degradation by ozonation: Kinetics, phosphorus transformation, anti-precipitation property changes and phosphorus removal. *Water Res.* 2019, 148, 334–343. [CrossRef]

20. Wang, L.T.; Ge, H.H.; Han, Y.T.; Wan, C.; Sha, J.Y.; Sheng, K. Effects of Al$_2$O$_3$ nanoparticles on the formation of inorganic scale on heat exchange surface with and without scale inhibitor. *Appl. Therm. Eng.* 2019, 151, 1–10. [CrossRef]
21. Wang, F.; Ge, H.H.; Wu, K.; Wang, L.T.; Wan, C.; Sha, J.Y.; Zhao, Y.Z. Effects of Al₂O₃ nanoparticles on the crystallization of calcium carbonate in aqueous solution. *J. Nanosci. Nanotechnol.* **2019**, *19*, 3471–3478. [CrossRef] [PubMed]

22. Tang, J.; Cao, D.; Wang, Y.; Mohamad, C.; Chen, L.; Wang, H. Research on Growth Behavior of Calcium Carbonate Scale by Electrochemical Quartz Crystal Microbalance. *Int. J. Electrochem. Sci.* **2017**, *12*, 11955–11971. [CrossRef]

23. Kiaei, Z.; Haghtalab, A. Experimental study of using Ca-DTPMP nanoparticles in inhibition of CaCO₃ scale. *J. Appl. Polym. Sci.* **2019**, *136*, 44740. [CrossRef]

24. Cui, K.; Li, C.; Yao, B.; Yang, F.; Sun, G. Synthesis and evaluation of an environment-friendly terpolymer CaCO₃ scale inhibitor for oilfield produced water with better salt and temperature resistance. *J. Appl. Polym. Sci.* **2020**, *137*, 48460. [CrossRef]

25. Oshchepkov, M.; Kamagurov, S.; Tkachenko, S.; Ryabova, A.; Popov, K. Insight into the Mechanisms of Scale Inhibition: A Case Study of a Task-Specific Fluorescent-Tagged Scale Inhibitor Location on Gypsum Crystals. *ChemNanoMat* **2019**, *5*, 586–592. [CrossRef]

26. Shen, Z.; Li, J.; Xu, K.; Ding, L.; Ren, H. The effect of synthesized hydrolyzed polymaleic anhydride (HPMA) on the crystal of calcium carbonate. *Desalination* **2012**, *284*, 238–244. [CrossRef]

27. Kiae, Z.; Haghtalab, A. Experimental study of using Ca-DTPMP nanoparticles in inhibition of CaCO₃ scaling in a bulk water process. *Desalination* **2014**, *338*, 84–92. [CrossRef]

28. Yang, X.; Huang, W.; Li, Y.; Wang, S. CaCO₃ crystallization in 2, 3-epoxypropyltrimethylammonium chloride modified gelatin solutions. *Powder Technol.* **2017**, *320*, 368–376. [CrossRef]

29. Nada, H.; Nishimura, T.; Sakamoto, T.; Kato, T. Heterogeneous growth of calcite at aragonite {001}-melt interfaces: A molecular dynamics simulation study. *J. Cryst. Growth* **2016**, *450*, 148–159. [CrossRef]

30. Miyazaki, T.; Arii, T.; Shirosaki, Y. Control of crystalline phase and morphology of calcium carbonate by electrolysis: Effects of current and temperature. *Ceramics International*. *Ceram. Int.* **2019**, *45*, 14039–14044. [CrossRef]

31. Ma, Y.F.; Gao, Y.H.; Feng, Q.L. Effects of pH and temperature on CaCO₃ crystallization in aqueous solution with water soluble matrix of pearls. *J. Cryst. Growth* **2010**, *312*, 3165–3170. [CrossRef]

32. Reis, M.C.; Sousa, M.F.B.; Aloibad, F.; Bertran, C.A.; Wang, Y. A two-fluid model for calcium carbonate precipitation in highly supersaturated solutions. *Adv. Powder. Technol.* **2018**, *29*, 1571–1581. [CrossRef]

33. Polat, S. Evaluation of the effects of sodium laurate on calcium carbonate precipitation: Characterization and optimization studies. *J. Cryst. Growth* **2019**, *508*, 8–18. [CrossRef]

34. Chaussemier, M.; Pourmohtashem, E.; Gelus, D.; Pécoul, N.; Perrot, H.; Lédion, J.; Horner, O. State of art of natural inhibitors of calcium carbonate scaling. *Desalination* **2015**, *356*, 47–55. [CrossRef]

35. Liu, C.; Zhang, W.; Li, H. Selective flotation of apatite from calcite using 2-phosphonobutane-1, 2, 4-tricarboxylic acid as depressant. *Miner. Eng.* **2019**, *136*, 62–65. [CrossRef]

36. Ji, Y.; Chen, Y.; Le, J.; Qian, M.; Huan, Y.; Yang, W.; Chen, Y. Highly effective scale inhibition performance of amino trimethylene phosphonic acid on calcium carbonate. *Desalination* **2017**, *422*, 165–173. [CrossRef]

37. Gopi, K.; Subramanian, V.K. Polymorphism in CaCO₃—Effect of temperature under the influence of EDTA (di sodium salt). *Desalination* **2012**, *297*, 38–47. [CrossRef]

38. Wen, R.M.; Deng, S.Q.; Zhu, Z.L.; Fan, W.; Zhang, Y.F. Studies on complexion of ATMP, PBCTCA, PAA and PMAAA with Ca²⁺ in aqueous solutions. *Chem. Res. Chin. Univ.* **2004**, *20*, 36–39.

39. Demadis, K.D.; Lykoudis, P.; Raptis, R.G.; Mezei, G. Phosphonopolycarboxylates as chemical additives for calcite scale dissolution and metallic corrosion inhibition based on a calcium-phosphonotricarboxylate organic-inorganic hybrid. *Cryst. Growth Des.* **2006**, *6*, 1064–1067. [CrossRef]

40. Popov, K.; Rudakova, G.; Larchenko, V.; Tushchev, M.; Kamagurov, S.; Dikareva, J.; Kovaleva, N.A. Comparative Performance Evaluation of Some Novel “Green” and Traditional Antiscalants in Calcium Sulfate Scaling. *Mat. Sci. Eng.* **2016**, *2016*. [CrossRef]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).