Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27439

226 (2021) 9–14
June

Study of scale inhibitor SI-4497 effect on calcareous deposit

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Received 7 March 2021; Accepted 18 May 2021

ABSTRACT

Calcareous deposits in water desalination generate serious problems and lead to considerable economic losses. The aim of this study is to investigate the inhibition of calcareous deposits using polyphosphonate (scale inhibitor SI-4497), which is an ideal additive for desalination operations. We studied the recovery rate of titanium electrode, in the presence and absence of this inhibitor, using chronoamperometry. A cathodic potential of –1.3 V/SCE (SCE – saturated calomel electrode) is used at 1,000 rpm and at 20°C, 40°C, 60°C, 80°C. Levich's law is verified before and after 1 h of electrodeposition in presence of an inhibitor. It was found that electrode recovery decreases with the addition of 3.5 ppm polyphosphonate (scale inhibitor SI-4497), resulting in an efficiency of 63.65%.

Keywords: Calcareous deposit; Chronoamperometry; Natural seawater; Inhibitor; Levich Law

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1. Introduction

Calcareous deposit (mixture of calcium carbonate and magnesium hydroxide) [1–3] observed in numerous industrial installations with seawater circulation is a serious problem since it can limit exploitation [4–8]. The calcareous deposit formed at the heat exchanger in the desalination circuit must be avoided. The most adequate solution for this is to inject inhibitors into raw water. Products used are as follows:

Polyphosphates: According to Larson [9], polyphosphate addition to water at a threshold concentration inhibits calcium carbonate crystal growth. However, polyphosphates become ineffective in presence of magnesium ions. Himelstein and Amjad [10] have emphasized that these products are effective and inexpensive, and they may eventually form orthophosphate deposits as a result of hydrolysis phenomena. According to Boffardi [11], polyphosphates hydrolyze from 70°C in shorter chains depending on water pH to an ionic form of orthophosphate PO_4^{3-}, losing their inhibitory effect. In addition, orthophosphates lead to insoluble deposits of $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$.

Organophosphonates: These compounds have phosphorus-carbon (P–C) bonds that are more resistant to hydrolysis than P–O bonds in polyphosphates [12]. Organophosphonates are chelation inhibitors, their property consists in inserting metal ions into their own molecular structures as shown by Lacour et al. [13], and they inhibit deposition crystal growth. Phosphonates have a wide application in cooling water, desalination systems and oil installations [14].

Carboxylic polymers: effective on most calcareous deposits, and don't cause a problem for rejects. They have the disadvantage of being costly.

Acid cleaning: causing bicarbonate decomposition, is another effective way to prevent deposits (reaction 1).

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$$H^+ + HCO_3^- \leftrightarrow CO_2 + H_2O \quad (1)$$

This cleaning process is obtained by circulating a dilute acid solution through a loop to be cleaned [15].

The aim of this study is to follow calcareous deposit on titanium surface as a working electrode by chronoamperometry, in the presence and absence of a polyphosphonate inhibitor (SI-4497 scale inhibitor) [16].

2. Material and methods

The solution used comes from natural seawater (NSW) and has characteristics shown in Table 1. This water is taken from the desalination circuit supply point of Cap Djinet Power Plant, that is, it has received preliminary treatment; it has considerable salinity and is loaded with calcium and magnesium cations responsible for its hardness.

To avoid the formation of calcareous deposit, polyphosphonate (SI-4497 scale inhibitor) has been tested [16]. It's a commercial chemical additive whose exact composition is unknown. This required us to consider the physical nature of the product (liquid or solid) in estimating added inhibitor quantities. Their main characteristics are shown in Table 2.

Electrochemical tests were carried out using a Potentiostat/Galvanostat (PGP 201 of Analytical Radiometer mark, controlled by a Voltmaster 4 software to record polarization and chronoamperometric curves. The working electrode was connected to a rotary system (speed control unit), and we manually controlled its rotation speed (Ω). Titanium working electrode had an active surface of 7.06 mm^2, on which calcareous deposit formed at different potential values during 1 h. Reference electrode is saturated calomel electrode (SCE) [17]. The grade of titanium used is grade 2 with a purity of 99.2% [18]. The active surface of a titanium electrode was prepared by polishing on silicon carbide (SiC 1200) abrasive paper (14 μm), followed by placing in acetone for 10 min and then in 40% ethyl alcohol for 15 min. In order to reduce an oxide layer that forms on titanium surfaces in free air, electrochemical polishing in Milli-Q water was necessary [19]. As the last step, a 5 min degassing at –2.5 V/SCE was carried out before starting the chronoamperometric test.

3. Results and discussions

3.1. Verification of Levich Law

3.1.1. Before electrodeposition

To verify the nature of the transfer regime during the use of the scale inhibitor and to estimate electrode recovery, we verified Levich's Law [20]. In fact, we have followed changes in current density as a function of the square root of electrode rotation speed in NSW, in the presence and absence of inhibitor polyphosphonate at a temperature of 20°C. The tests are performed on the bare electrodes, that is, before deposition formation. The traces obtained are shown in Fig. 1. Current density plotted as a function of the square root of electrode rotation speed: $I = f(\Omega^{1/2})$ give straight lines in presence and absence of inhibitor. This indicates that diffusion governs the transfer regime [21].

In the presence of polyphosphonate inhibitor, obtained straights have slopes that increase with inhibitor concentration. These results show that reduced electrode surface active area is achieved with an increased amount of inhibitor. Knowledge of slopes of these lines allows us to estimate electrode recovery rate R (%) according to Eq. (2).

$$R(\%) = \frac{K_0\ \text{ppm} - K_x\ \text{ppm}}{K_0\ \text{ppm}} \times 100 \quad (2)$$

where K_0 ppm and K_x ppm are slopes of bare electrode lines without and with inhibitor, respectively.

Table 2
Typical physical properties of commercial scale inhibitor used

Appearance	Clear colorless liquid
Density (kg/m^3 at 25°C)	1,030–1,120
Flash point (°C)	–
Boiling point (°C)	>100
Melting point (°C)	<0
pH concentrated	6–7
Solubility	Water soluble

Table 1
Physicochemical analyses of NSW from desalination circuit supply point of Cap Djinet Power Plant at 20°C

Parameter	Value	Parameter	Value
pH	7.79	SiO_2 (mg/L)	0.057
Electrical conductivity (mS/cm)	52.4	Fe^{2+} (mg/L)	0.027
Salinity (g/L)	35.3	Na^+ (mg/L)	10,547
Hydrotimetric title TH (°F)	706	K^+ (mg/L)	589.2
Calcium hardness $TH_{Ca}{}^{2+}$ (°F)	301	Sr^{2+} (mg/L)	9.5
Magnesium hardness TH^{2+}_{Mg} (°F)	405	SO_4^{2-} (mg/L)	3,045
Alkalimetric title TA (°F)	0.8	HCO_3^- (mg/L)	123.41
Full alkalimetric TAC (°F)	13.67	Chemical oxygen demand (mg/L)	2,507
Cl^- (mg/L)	19,680		

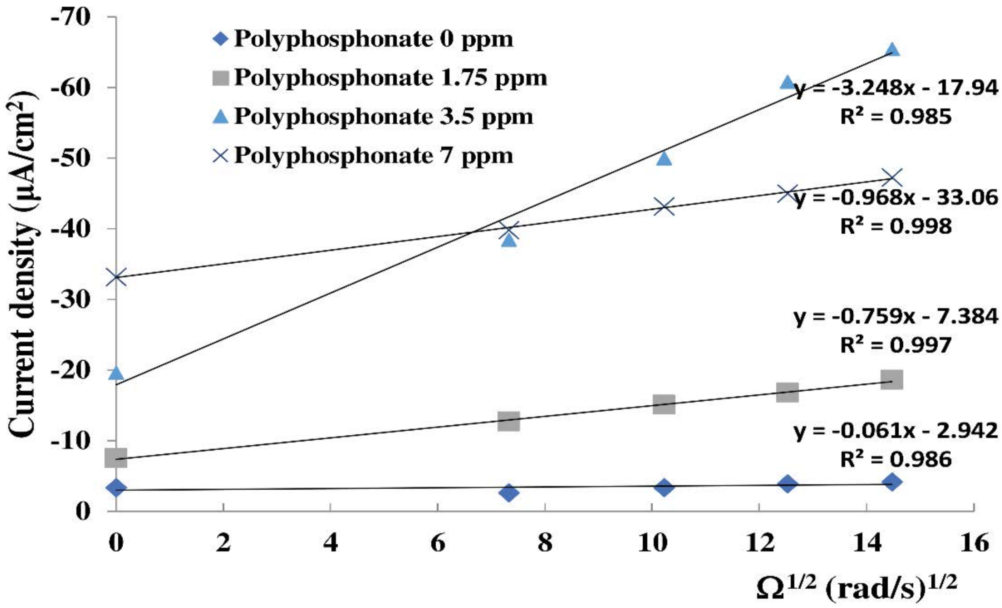

Fig. 1. $I = f(\Omega^{1/2})$ for different concentrations of polyphosphonate at 20°C and before electrodeposition.

According to Table 3, we recorded a polyphosphonate recovery rate of titanium electrode that increases with increasing concentration and reaches 52.24% for a 7 ppm dose. This proves that polyphosphate acts before germination of calcareous formation.

3.1.2. After 1 h electrodeposition

We also verified a diffusion regime for inhibition of calcareous deposit by polyphosphonate after 1 h of electrodeposition. Deposit formation was carried out using NSW solution at 20°C, with 1,000 rpm agitation and different polyphosphonate concentrations of 0, 1.75, 3.5 and 7 ppm.

Fig. 2 shows all results. We note the graphs of I according to Ω½ show straight lines for all concentrations cited above, thus indicating that the transfer regime is governed by mass transfer [21]. Contrary to what we have seen in the previous section on the bare electrodes (before electrodeposition), we note here that line slopes decrease in presence of inhibitor. Values of recovery rates are summarized in Table 4.

Indeed, after 1 h of electrodeposition, the electrode recovery rate becomes low compared to the initial time, which explains deposit friability by the addition of an inhibitor whose role is to change the crystalline form of deposit.

3.2. Chronoamperometry

3.2.1. Influence of concentration

Table 3
Recovery rate % of bare electrode in presence of polyphosphonate (scale inhibitor SI-4497)

Polyphosphonate concentration (ppm)	Recovery rate (R %)
1.75	11.44
3.5	14.86
7	52.24

Chronoamperometry was performed under the following operating conditions: a temperature of 20°C, a rotation speed of 1,000 rpm and a period of 1 h. Samples studied have increasing contents of polyphosphonate inhibitor of 0–7 ppm. The curves in Fig. 3 correspond to the deposition of NSW in polyphosphonate. The scaling time (t_S) defined by the intersection of the tangent line at the inflection point of each chronoamperometric curve with the abscissa axis, is short and residual current (i_{res}) is low in absence of inhibitor [22]. By contrast, t_S increases with the concentration of polyphosphonate and i_{res} increases and achieves values which remain almost constant after 40 min $100\ \mu\text{A/cm}^2 < i_{\text{res}} < 200\ \mu\text{A/cm}^2$. Electrodeposition kinetics are slowed and its mechanism is changed [23–25]. Fluctuations curves observed possibly related to detachment deposit. Inhibitor efficiency IE % can be calculated by the following relationship.

$$\text{IE\%} = \frac{t_{S0} - t_{\text{Sinhi}}}{t_{S0} + t_{\text{Sinhi}}} \times 100 \tag{3}$$

where t_{S0} and t_{Sinhi} are times scaling in absence and in presence of inhibitor, respectively. Efficiency values for each inhibitor content are illustrated in Table 5.

By analyzing these results, we see that calcareous deposit is slowed down by polyphosphonate inhibitor. This is due to fact that time scaling (t_S) increased by a

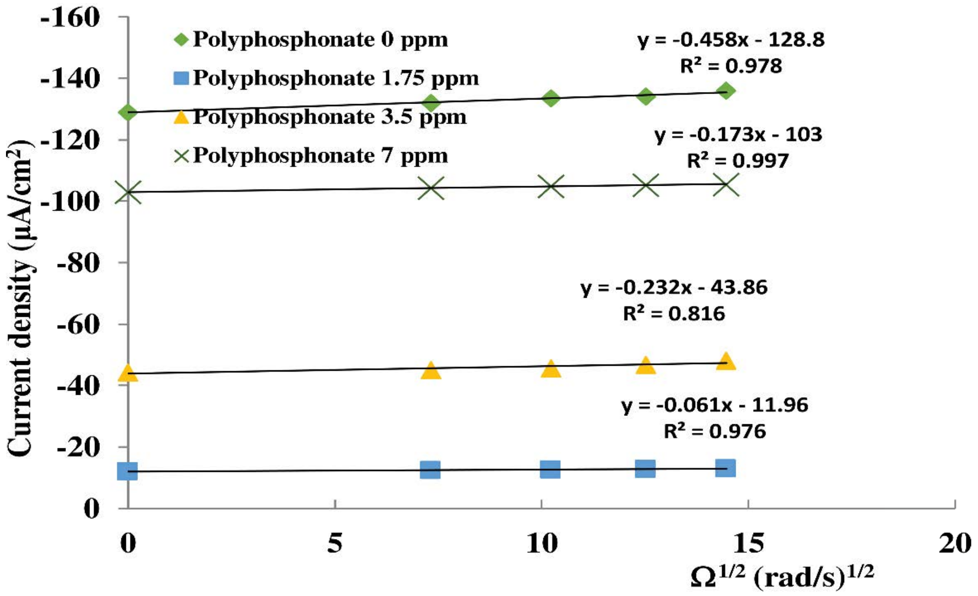

Fig. 2. $I = f(\Omega^{1/2})$ for various concentrations of polyphosphonate at 20°C and after 1 h electrodeposition.

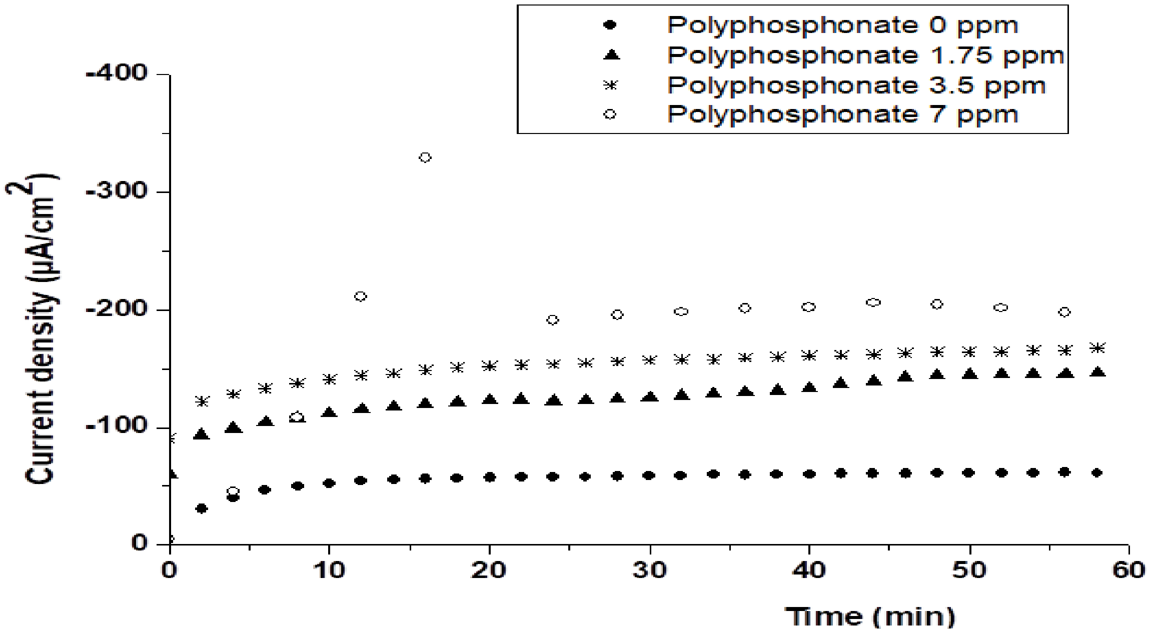

Fig. 3. Influence of polyphosphonate concentrations on calcareous deposit in NSW at 20°C, 1,000 rpm and –1.3 V/SCE.

Table 4
Recovery rate (*R* %) of electrode after 1 h electrodeposition in presence of polyphosphonate (scale inhibitor SI-4497)

Polyphosphonate concentration (ppm)	Recovery rate (*R* %)
1.75	0.86
3.5	0.49
7	0.62

Table 5
Time scaling (t_s) values and efficiency inhibitor (IE %) utilized

Deposit at 60 min (ppm)	0	1.75	3.5	7
t_s (min)	10	20	30	40
IE (%)		33.33	50	63.63

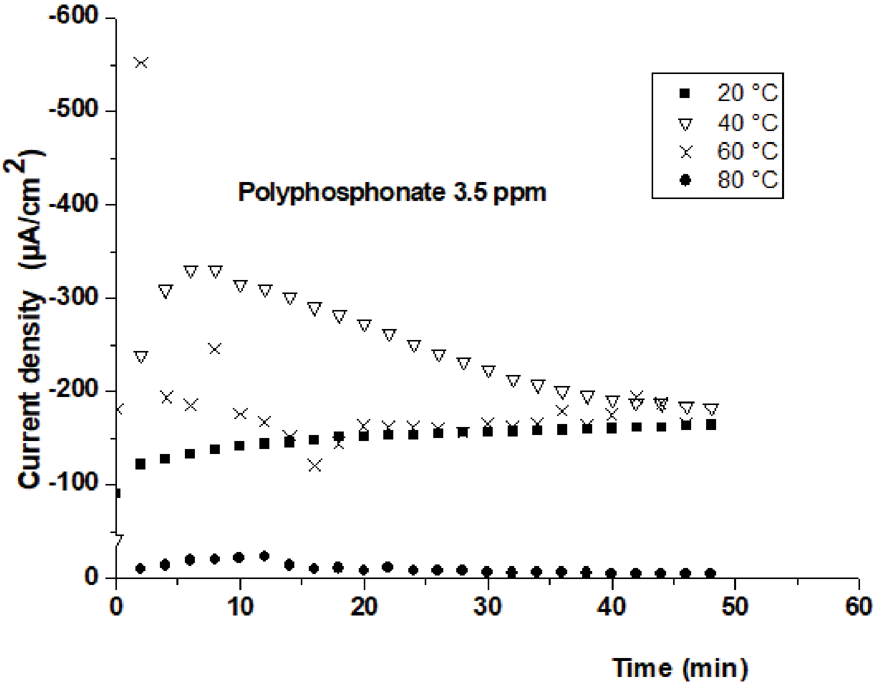

Fig. 4. Influence of temperature on calcareous deposit in NSW in presence of phosphonate at 3.5 ppm, 1,000 rpm, –1.3 V/SCE.

factor of four for a 7 ppm dose of polyphosphonate compared to its absence.

3.3. *Influence of temperature*

Temperature is one of most important parameters that affect calcareous electrodeposition kinetics [26–28]. It affects motor of this process which is hydroxyl OH^- ions production, which is responsible for germination and growth of calcareous deposit. Therefore, studying polyphosphonate (scale inhibitor SI-4497) effect on deposition over a temperature range of 20°C–80°C becomes essential.

In Fig. 4, we notice that scale time t_S increases with increasing temperature for a 3.5 ppm of inhibitor. This is very remarkable at temperatures >20°C. Moreover, current density range at these temperatures is much higher than 20°C. This reveals a slowing down of kinetics of calcareous deposit by phosphonate adsorption on surface electrode. These results are in accordance with previous work by Zidoune et al. [29].

4. Conclusions

The tracing I according to $\Omega^{½}$ (Appliquation's Levich Law) gives straight lines in the absence and presence of inhibitor. Indicating that the transfer regime is governed by diffusion. Knowledge of straight-line slopes allows us to estimate the recovery rate electrode which becomes low by adding inhibitor. In fact, for 3.5 ppm dose of polyphosphonate after 1 h electrodeposition, recovery rate electrode by calcareous deposits is respectively 0.49%, 0.45% and 0.05%. The anti-deposit effect of polyphosphonate inhibitor was demonstrated by chronoamperometry. This allowed us to calculate its efficiency in order of 63.63% for a required amount of 3.5 ppm.

A study of temperature influence showed that residual current of calcareous deposit after 1 h in presence of polyphosphonate inhibitor increase with increasing temperature. This is explained by polyphosphate is an efficient anti-deposit at high temperatures.

Acknowledgments

The authors would like to acknowledge the Algerian Institute of Oil, IAP Boumerdes-Algeria for chronoamperometry measurements.

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