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Elucidation of dual-mode inhibition mechanism of a typical polymer-based antiscalant on Red seawater for thermal desalination at higher temperatures and higher concentration factors

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Title : Elucidation of dual-mode inhibition mechanism of a typical polymer-based antiscalant on Red seawater for thermal desalination at higher temperatures and higher concentration factors

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Highlights

- Scaling and its demerits to thermal desalination at higher temperature
- Inhibition and mitigation of the scales with polymeric antiscalant
- Spectacular display of threshold mechanism with solution chemistry
- Induction of distorted crystal deposition from antiscalant interaction

Graphical abstract

Abstract

Scale deposition in the thermal process for desalination is quite inevitable. This study is about scale formation, crystal modification, and prevention mechanism of a tetrapolymer based antiscalant on Red Seawater. Red seawater at concentration factors (CF) of 1.5 and 2.5 was studied under reflux condition at 70°C and 98°C respectively for seven hours with 1ppm, 2ppm, and 4 ppm concentration of the antiscalant. Eventually, the mechanism of inhibitory action of the antiscalant has been reconnoitered after seawater analysis and imaging the morphological changes in the crystal formation patterns with Scanning electron microscope (SEM). The changes in the values of pH, turbidity and alkalinity (both phenolphthalein alkalinity (PA) and total alkalinity (TA)) were measured to apprehend various fluctuations happening as a result of the addition of antiscalant. The variations in the pH of seawater with antiscalant were in concurrence with the changes in alkalinity and was also reflected in turbidity. These changes explicitly demonstrated the threshold mechanism of scale inhibition. SEM micrographs exhibited distorted round shaped depositions supporting crystal modification mechanism as well. The efficiency and dominance of inhibitory mechanism varied from 2 hours to 6 hours for the antiscalant and was observed to be directly related to CF of seawater used, the temperature applied, and a dose of antiscalant added.

Key Words: Antiscalant, Scales, Inhibition, Seawater desalination, Threshold, Crystal modification

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1. Introduction

Seawater desalination is the most flourishing and well-established process of the day. It is highly anticipated to fulfill the gap of demand & supply of potable water for the success and sustainability of exponentially expanding socioeconomic structures (Gao et al., 2017) (Ghaffour et al., 2013; Ng et al., 2015; Shahzad et al., 2017) (Uhlenbrook and Connor, 2016) of the current world. In gulf region, thermal desalination is the most contributing process of desalination because of enough resources of energy source (Gao et al., 2017; Ghaffour et al., 2013) (viz., crude oil, natural gas) , adverse water quality (Dhakal et al., 2018; Manheim and Jiang, 2017; Shahzad et al., 2018; Villacorte et al., 2014) and huge need and demand for water in the arid climate (Ghaffour et al., 2014; Pfister et al., 2011). However, sea water is having lots of dissolved salts (Benjamin, 2010), so deposition of scales is quite obvious and evident in most of the thermal desalination plants (Abderrahim et al., 2016; Alahmad, 2008; Din et al., 2005; Dooly and Glater, 1972; Fellows and Al-Hamzah, 2015; Rahman and Amjad, 2010; Singh, 2017). It has negative consequences on the desalination process as it causes an increase in the specific energy consumption resulting in an overall reduction of water production. Therefore, overall efficiency and economy of the thermal desalination processes are anticipated to decline as a result of other additional costs incurred to pretreatment of water, cleaning and chemical treatments for scale removal, frequent operation termination to maintain the production of water to improve the energy transfer rate and water production (Bohnet, 1987; Bots et al., 2012; El-Dessouky and Khalifa, 1985; Fellows and Al-Hamzah, 2015; Gill, 1999; McCabe and Robinson, 1924).

Calcium carbonate is one of the most abundant minerals having a vital role in various natural, geochemical and bio-mineralization processes (Teng et al., 2017). Similarly, there exists a delicate balance of calcium and CO_3^{--} in the seawater to support multiple natural phenomena and underwater life (Benjamin, 2010; Stumm, 1995). CaCO_3 formation in seawater is a result of

several chemical equilibria viz., dissolution of CO_2 gas, carboxylic acid formation, dehydration of carboxylic acid, protonation of CO_3^{2-} ion, hydrolysis of calcium hydroxide and equilibrium between calcium and carbonate as depicted in equations 1-5 (Al-Rawajfeh et al., 2015; Alahmad, 2008; Benjamin, 2010).

Therefore, it is expected and quite impossible in the water industry, especially thermally driven processes to remain unaffected by scale deposition (Bohnet, 1987; Budhiraja and Fares, 2008; Dooly and Glater, 1972; Fellows and Al-Hamzah, 2015; Gill, 1999; Hamrouni and Dhahbi, 2001; Hasson et al., 1968; Kazi et al., 2012; McCabe and Robinson, 1924; Neville and Morizot, 2000; Rahman and Amjad, 2010). Most prominent scale formed in the water (seawater) industry is of CaCO_3 , though calcium sulfate is formed at a relatively higher temperature ($>110^\circ\text{C}$) (Alahmad, 2008; Andritsos and Karabelas, 2003; Benjamin, 2010; Budhiraja and Fares, 2008; Dooly and Glater, 1972; Hamrouni and Dhahbi, 2001; Harris et al., 1974; Hasson et al., 1968; Hoang, 2015b; Langelier et al., 1950; McCabe and Robinson, 1924; Rahman and Amjad, 2010; Sousa et al., 2016; Zhang et al., 2015).

Pretreatment/modification of feed water and use of the scale preventing chemicals (antiscalants) are the two most commonly used techniques to counter the scaling in the water

industry (Al-Hamzah and Fellows, 2015; Al-Sofi et al., 1998; Ayoub et al., 2014; Chaussemier et al., 2015; Chernozubov et al., 1966; Cho and Kim, 2015; Dunseth et al., 1964; Linnikov et al., 1989; Neville and Morizot, 2000; Sano and Nakashima, 2018; Vidic et al., 2015). Both methods have their pros and cons depending on the various aspects of a particular technology to be used for, and quality of water and application. The most anticipated and effective way to counter scaling is the use of scale preventing chemicals/ antiscalants. Use of antiscalants require quite a low dosage and is quite reliable and effective without compromising the water quality, thus have the upper hand with respect to pretreatment.

In general, scale formation is a quite complex phenomenon where various anions and cations under certain driving forces/ conditions viz. temperature, pressure, pH, the addition of some foreign solute/solvent, etc. come close enough electrostatically to result in a supersaturated solution. It leads to aggregation of the ions and causing nucleation. Henceforth, it grows in size due to the transportation of more ions pairs from the bulk solution to the site of nucleation and their adsorption on its surface, extending the size into a crystal (Fig. 1). Antiscalant, on the other hand, exhibit their scale preventing ability by inducing various physio-chemical alterations during scale formation directly or indirectly (Hoang, 2015a; Teng et al., 2016). It involves either engagement with particular scale forming ion/group of ions resulting in the delay in the mechanism responsible for scale formation or involvement in such a way not to allow to adherence/deposition of scales on the surface responsible and to be affected the most (Chauhan et al., 2015). There are three most accepted mechanism as shown schematically in figure 1, which are believed to describe them the best are: 1. The threshold effect; 2. Dispersion, and 3. Crystal modification.

The threshold mechanism plays its inhibitory action prior to the inception of ions precipitation and prevents scale formation. It tends to disturb the ionic product of the participating ions to not

119 to reach to their solubility product which is responsible for their pairing and aggregation leading
 120 and nucleation is prevented. Hence, scale formation is delayed/ inhibited.

Figure 1 Schematic representation of the inhibitory mechanism of antiscalant

123 If the threshold mechanism doesn't come into action, then dispersion and crystal modification
 124 are the other two ways to prevent scaling. The ions combine to precipitate, but the nature of
 125 agglomeration of participating ionic species follows the preventive mode of scale formation by
 126 following two different means depending on the chemical nature of the scale inhibitors. It might
 127 be adsorbed on the surface of the precipitates/ nuclei; thus incorporating the charged species
 128 on the surface. This makes the agglomerate/ microcrystals to repel each other. Hence,
 129 microcrystal formed are dispersed by the charge incorporated, and scaling is prevented. The
 130 second mode of its inhibitory action is by becoming the part of the active crystal lattice itself
 131 during crystal growth. The antiscalant occupies one of the space lattices in the crystal. Thus
 132 crystals will be formed, but the growth of the overall crystal will be hampered and slanted, or an
 133 irregular growth is induced. Consequently, the scales deposition becomes very brittle and

unstable as a result of higher internal stresses in the distorted crystal; hence scaling effect is mitigated.

There have been many research group working on the development of various antiscalant and their efficiencies for scale inhibition (Al-Rawajfeh et al., 2015; Boels and Witkamp, 2011; Chen et al., 2015; Gallup and von Hirtz, 2015; Kazi et al., 2012; Li et al., 2015; Patel and Finan, 1999; Rahman and Amjad, 2010; Sheikhi et al., 2016; Singh, 2017; Teng et al., 2016; Vidic et al., 2015), but there are few studies which are exploring the higher concentration of feed water (conc. seawater/ brine) and extended temperature conditions into the account (Ketrane et al., 2009). The primary objective of this work is to comprehend various transitions happening in the bulk solution after addition of tetrapolymer based antiscalant to concentrated Red seawater. This study is to evaluate and correlate these changes which influence the scale formation and to explore the mode of its inhibitory mechanism at a higher temperature. The efficacy of the antiscalant has been already studied and reported for Red seawater in the previous work (Singh, 2017). The experiment is professed to simulate the condition of a thermally operated desalination plant with exceptional higher feed water concentration and higher temperature.

2. Experiment

2.1. Materials and methods

Fresh Red seawater was used for experiment to have a tangible understanding of the scale preventive mechanism of the antiscalant. The experimental conditions and experimental setup were kept the same as reported elsewhere (Singh, 2017). The seawater was collected and filtered through 0.5-micron filter to screen out all the particulates, which could impact the scale formation. It was concentrated in the rotatory vapor (Buchi) instrument at 30°C and 20 mbar pressure to avoid any scale formation. The assorted concentration factor (CF) of 1.5 and 2.5 were achieved by adjusting the conductivity either by adding fresh seawater to the concentrated

one or by further concentration of seawater. The initial pH and conductivity values of concentrated seawater solution were measured. A stock solution of 400 ppm (w/w) for antiscalant as of product concentration was prepared in deionized water. The concentrations of antiscalant to be studied were maintained at 0ppm, 1ppm, 2ppm, and 4ppm. The scaling experiment was conducted under reflux conditions as depicted in figure 2. The experiments were repeated thrice to confirm the reproducibility of the results. 400 ml of concentrated seawater of defined CF was heated in round bottle flasks with a predefined dosage of antiscalant at a controlled temperature of 70°C and 98°C in an oil bath with continuous stirring at 500 rpm for 7 hours. A piece of stainless steel coupon of dimension 1cm x 1cm was used to allow the scales to deposit on its surface to study and evaluate the morphology of the scales deposited and the effect of the addition of antiscalant on them.

Figure 2 Schematic of the experimental set up to understand scaling and inhibition mechanism of antiscalant

During the experiment, 15 ml of seawater solution was pipetted out after every half an hour to measure the pH and alkalinity. In the meantime, turbidity was also measured in turbidity meter

from the aliquot taken separately and poured back into the original solution. Titration method was used to measure the alkalinity change with time. Alkalinity being very comprehensive is measured for the total concentration of OH^- ions, CO_3^{--} ions, and HCO_3^- present in the solution. Therefore, phenolphthalein solution and mixed indicator were used to obtain different inflection point in sequence to understand various equilibrium shifts responsible for scale formation and its prevention. After completion of 7 hours, coupons were taken out of the solution and rinsed with deionized water to prevent any salt deposition. These coupons were dried and coated with Iridium (4nm) under vacuum in sputter coater and were examined with Scanning Electron Microscope/ Energy Dispersive X-Ray Analysis (SEM/EDAX)(FEI Quanta 600 FE-SEM) for the morphology and elemental composition of the scales deposited.

2.2. Theory

The most common scale deposition in the water industry is of CaCO_3 . As explained, there exists a delicate equilibrium in the seawater which is very crucial for various biochemical phenomena prevalent in the oceans and is vital to prevent the scaling. Any change or deviation in the condition to maintain this coexistence of various ionic species in equilibrium could disturb this delicacy and might result in the shifting of the reaction in either direction. Scale formation is a result of this disturbance of the equilibrium and thus accelerates the combination of the participant ions to form precipitates irreversibly and are deposited as scale; though, there are various theories reported for scale formation in seawater and were related to these equilibria (Alahmad, 2008; Amjad, 2015; Dooly and Glater, 1972; Hasson et al., 1968; Langelier et al., 1950). In one of the earliest reported theory (Langelier, 1954; Langelier et al., 1950), scale formation starts with thermal decomposition of HCO_3^- ion to produce CO_3^{--} ions as depicted in equation 6. In another approach (Dooly and Glater, 1972), HCO_3^- ion first thermally degenerate to hydroxide ion which further reacts to produce CO_3^{--} ions as illustrated in equations 8-9.

204

205 In thermal desalination processes, as seawater starts getting heated, the HCO_3^- equilibrium is
 206 disturbed and shifted in the forward direction to produce more CO_3^{2-} ions and releasing carbon
 207 dioxide gas (Langelier, 1954). As a result, the ionic concentration of the CO_3^{2-} species
 208 increases system and hence, pushes the reaction responsible for consuming the excess CO_3^{2-}
 209 ions to combine with calcium ions to precipitate. This counteraction of neutralizing the excess
 210 CO_3^{2-} acts as a catalyst for further dissociation of carbonic acid to HCO_3^- ions and hence
 211 overall system shifts in the forward direction resulting in more precipitates formation. Meanwhile,
 212 the concentration of hydroxide ions keeps on increasing until the solubility product of
 213 magnesium ions and hydroxide ions is achieved, and hereafter magnesium hydroxide scale
 214 starts depositing as depicted in Eq. 11.

216

217 3. Results & Discussion

218 3.1 Physio-Chemical analysis

Scale formation involves lots of complex phenomena. As explained earlier in the theory section, there are various equilibrium system in the seawater, which gets disturbed and leads to scaling. These shifts in the equilibrium can be observed and recorded by measuring different physio-chemical properties viz. pH, alkalinity, and change in the turbidity of the solution. These elucidate various inter-related changes happening in the scaling phenomenon and are explored for Red seawater with a predefined dose of antiscalants and concentration of seawater at 70°C and 98°C.

Figure 3. Seawater variation at 70°C for CF 1.5 with respect to (a) pH (solid lines) and phenolphthalein alkalinity (dotted lines) and (b) total alkalinity (solid lines) and turbidity (dotted lines)

Figures 3 and 4 depict various changes happening in the solution at 70°C for assorted doses of antiscalant with seawater CF of 1.5 and 2.5. It was observed that the value of pH and PA go in parallel as if in a synchronized manner. The value of pH remained nearly constant for 200 minutes (approx.) for seawater with CF 1.5 in baseline condition as depicted in figure 3(a). PA also followed the same trend. Henceforth, both PA, as well as pH, started declining. While the value of pH and PA were observed to increase for seawater with antiscalant, however, it's quite interesting to find that TA was nearly constant for the solutions with antiscalant (figure 3(b)). The sudden change in the turbidity was also seen only after same inflection point of decline in pH value for baseline condition, whereas it was quite moderate and delayed for other solutions (figure 3(b)). Though, the change in the value of turbidity for the solution with 1 ppm antiscalant dose was observed to start earlier around 250 minutes than others solutions where it was found to increase only after 350 minutes with an antiscalant dose of 2ppm and 4 ppm.

Figure 4. Seawater variation at 70°C for CF 2.5 with respect to (a) pH (solid lines) and phenolphthalein alkalinity (dotted lines) and (b) total alkalinity (solid lines) and turbidity (dotted lines)

Figure 4(a) depicts that the value of pH and phenolphthalein alkalinity declined immediately for the seawater with CF 2.5 at 70°C. Whereas, pH value started declining after around 60 minutes, which became quite prominent after approximately 160 minutes of heating the solution with a 1ppm concentration of antiscalant. For the solutions with 2 ppm and 4 ppm antiscalant dosage, the value of PA showed a slight increase with time, though it was more prominent with 2 ppm as depicted in figure 4(a). Turbidity was also observed to increase similarly with the respective inflection point of change in the value of pH and PA for baseline and 1ppm antiscalant solution, as shown in figure 4(b). Similarly, TA decline was also observed to be consistent with pH change for baseline, and 1 ppm solution but this drop was observed to be quite feeble for solutions with 2ppm and 4ppm antiscalant doses.

As discussed in the theory section that there is a shift in the equilibrium with an increase in the temperature of seawater solution, the concentration of HCO_3^- ions start to decline as equilibrium tends to move in a forward direction with the heating of the solution as shown in Eq. 6 & 9. It leads to the formation of CO_3^{2-} ions. Therefore, the concentration of CO_3^{2-} ions reaches the level to exceed the solubility product along with calcium ions to form CaCO_3 scale. At 70°C, it

took nearly 200 minutes for seawater with 1.5 CF to exceed solubility product of the two to induce scales. Once it was achieved, ions started to aggregate, and precipitation happened. Therefore, an abrupt change in the value of turbidity, and a similar decline in TA of the solution was also observed (figure 3(b)). The change in the value of pH and PA can be attributed to dissociation of HCO_3^- ions to produce hydroxyl ions contributing to the increase in the PA (Eq. 8). The production of hydroxyl ions initiates further dissociation of HCO_3^- ions to form CO_3^{--} ions in baseline condition to aggregate as CaCO_3 (Eq. 9 & 10). However, the addition of antiscalant in the seawater seems to alter this step and delays the saturation point by masking the calcium ions, not allowing further aggregation with CO_3^{--} ions by altering the solubility limit. It acts as a threshold barrier, not allowing the two ions to combine. The addition of antiscalant tends to interfere, not to allow the two ions to form CaCO_3 scales and resulting in suppression of Eq. 9 for further carbonate production and advancement of Eq. 8 to produce more hydroxyl ions. Thus, an increase in pH and PA were observed for seawater with antiscalant (figure 3(a)). As a result, the overall alkalinity of the solution remains nearly constant with the addition of antiscalant throughout the experiment (figure 3(b)). Only change occurred in the solution was that most of the HCO_3^- ionic species were dissociated to form hydroxyl ions. It was observed that 1 ppm concentration of antiscalant was enough to prolong the scaling in seawater with 1.5 CF for nearly 7 hours.

For the seawater with CF 2.5 at 70°C, the overall concentration of the ions are quite higher, and hence these changes are reflected comparatively faster and predominant. The value of pH and PA started declining immediately as the concentration of calcium, and CO_3^{--} ions were at the hinge to be pushed to saturation level to beat the solubility product of the two to form the scales, and heating of the solution just acted as a catalyst. The solution became turbid immediately as depicted in figure 4(b), thus resulting in agglomeration leading to scale formation. Meanwhile, the addition of antiscalant reflected the same stand of threshold barrier, not allowing the two

ions to form CaCO_3 scales. However, 1 ppm concentration of the antiscalant was observed to be capable of acting as a threshold barrier until 180 minutes and then resulted in the formation of the scale as reflected by changes in the values of pH, TA and turbidity (figure 4 (a & b)).

Figure 5. Seawater variation at 98°C for CF 1.5 with respect to (a) pH (solid lines) and phenolphthalein alkalinity (dotted lines) and (b) total alkalinity (solid lines) and turbidity (dotted lines)

The scale formation for seawater at 98°C for the assorted concentration of 1.5 and 2.5 CF were observed to be more prominent and vigorous. Figures 5 and 6 depict the various changes happening in the value of pH, phenolphthalein alkalinity, TA, and turbidity. For seawater with both CF of 1.5 and 2.5, the value of pH and PA declined immediately at 98°C in the baseline

condition. It can be attributed to the decomposition of HCO_3^- species as explained earlier to form CO_3^{--} ions and their aggregation with calcium ion to form CO_3^{--} precipitates.

Contrary to seawater at 70°C , the changes in the value of pH and PA were observed to be more prominent and profound due to a comparatively higher temperature (98°C) as depicted in the figures 3(a), 4(a), 5(a) and 6(a). Higher temperature accelerated the dissociation of the HCO_3^- ions much faster in the forward direction. The value of turbidity was also observed to be comparatively higher (approximately ten times) for the solution at this temperature. The presence of antiscalant in the solution showed the same inhibitory effect but to a minor extent. A similar trend of increase in the value of pH was observed for the solutions with antiscalants, but it was found to be of higher magnitude and protuberant at 98°C for corresponding CF of seawater. It directed the reactions in the forward direction relatively faster to form hydroxyl ions as shown in Eq. 8.

Figure 6. Seawater variation at 98°C for CF 2.5 with respect to (a) pH (solid lines) and phenolphthalein alkalinity (dotted lines) and (b) total alkalinity (solid lines) and turbidity (dotted lines)

The antiscalant dosage of 1 ppm was found to prolong the scaling process for approximately 100 minutes for seawater with CF of 1.5 (figure 5(a)), but it was not capable of doing the same for seawater with 2.5 CF (figure 6(a)) which was observed after around 20 minutes. At this dose of antiscalant, 2.5 CF seawater displayed a similar trend to baseline condition at 98°C exhibiting the reduction in retention time to scaling (figure 6(a)). The value of turbidity reflects that the scale formation was not much prominent as of baseline condition, as shown in figure 6(b). It took around 270 minutes to initiate precipitation in the solution with 2 ppm dose of antiscalant at 2.5 CF (figure 6), though TA was observed to decline with time immediate after 50 minutes suggesting the onset of scaling. But, this dosage was enough to extend the time to scale formation for the set condition of experiment duration of seven hours for 1.5 CF (figure 5). Though, overall alkalinity value started to decline after 170 minutes, indicates the decomposition of CO_3^{--} species at this condition. Thus, it is perceived to be optimal retention time with a 2ppm dose of antiscalant at 1.5 CF to avoid scaling at 98°C. There was a tremendous increase in the value of turbidity for the solution suggesting the ability of the antiscalant to disperse the crystals and not allowing them to deposit on the surface (figure 6(b)). No change was observed in the

value of TA for the solution with 4 ppm concentration of antiscalant for seawater with CF 2.5 reflecting its ability to hold scaling. However, there was an incremental increase in the values of pH and PA as explained due to the decomposition of HCO_3^- ions (Eq. 8), and it was relatively prominent for 2.5 CF seawater.

It's quite evident from the above analysis that heating caused the changes in the physio-chemical nature of the seawater solution. It initiated the dissociation of carbonate species (HCO_3^- ions and CO_3^{2-} ions), though the course of their reaction is still ambiguous whether it proceeded with the first approach as shown in Eq. 6 or followed the second approach as expressed in equations 8 & 9. From the above results, however, it seems that the addition of antiscalants followed the second approach more closely where HCO_3^- dissociates thermally into hydroxide ions. It is supported by an increase in the value of pH and PA, as explained earlier. It's quite clear that addition of antiscalant prologs the scale formation, which can be attributed to the 'threshold effect' as a result of the increase in the solubility limit of the ions. As a consequence, it was having enough time to further allow the dissociation of carbonate species to carbon dioxide and mitigated the scale formation. It was observed that the scale formation and their inhibition were proportionally related to CF of seawater, temperature, and dosage of antiscalant.

3.2. Morphological analysis

Stainless steel coupons were used to allow the scales to deposit on them. These were used to explore the effect of the antiscalant on the morphology of the scale; the coupons were analyzed with the help of scanning electron microscopy (SEM). SEM images revealed quite interesting changes in deposition patterns and gave a clear insight leading to the mechanism of antiscalant towards scale prevention. Figure 7 depicts the morphology of scales deposited from seawater at

70°C and 98°C with assorted concentrations of antiscalant. It is quite evident from the figure that there was no scale deposition for 1.5 CF seawater with various concentration of antiscalant except for a few but small and scattered granules of scales on the coupons. Crystals of CaCO_3 were observed for baseline solution without any additive. However, few flake shaped scales were also observed at 98°C baseline with magnesium as major constituent analyzed by EDAX. This observation is also supported by analysis of various changes in the value of pH, alkalinity, and turbidity from experimental seawater solution as explained in the analysis section.

The scale formation was observed to be relatively intense at 98°C for CF 1.5 seawater for baseline (figure 7). As inferred by the analysis of seawater solution, the scale deposition was expected with 1 ppm and 2 ppm dosage of antiscalant from the decline in the value of alkalinity. However, the extent of deposition of the scale was supposed to be prominent for seawater with 1 ppm antiscalant dose. A similar trend was also observed from the SEM images, as shown in figure 7. However, SEM images showed a few crystals of CaCO_3 but interestingly with a different morphology. These were observed to be round or sphere-shaped.

On the other hand, substantial-scale deposition was observed for seawater with 2.5 CF at 70°C and 98°C without antiscalant as depicted in figure 7. However, the scale formation was comparatively more intense for higher temperature (98°C). It is believed that higher temperature facilitates to acquire the activation energy to induce precipitation, and the movement and diffusion of the constituent ions accelerate to the scale formation sites from the bulk solution (Chauhan et al., 2015; Hoang et al., 2007). A similar trend was also observed in this study (figure 7). The composition of the scale was found to be different for the two from EDAX analysis. Most of the scales analyzed for 70°C for 2.5 CF were made of CaCO_3 while it showed different elemental constituents of calcium, carbon, sulfur, and magnesium, which were also reported in the previous study (Singh, 2017). At 70°C, for 2.5 CF seawater with 1 ppm of antiscalant, most of the crystals deposited were observed to be round shaped made up of

373 CaCO_3 . Though, no scale deposition was observed at higher dosage (2 ppm & 4 ppm) of
 374 antiscalant for same CF at this temperature (figure 7). For 2.5 CF seawater with 1 ppm
 375 antiscalant at 98°C , the scale deposition was not as intense as observed for baseline. However,
 376 the crystal deposited were of needle-shaped and round-shaped mostly made up of calcium
 377 sulfate and CaCO_3 , respectively (Singh, 2017). There was no needle-shaped crystal for
 378 seawater with 2ppm antiscalant at 98°C for 2.5 CF, but all were observed to be round shaped.
 379 However, no scale was observed with 4ppm of antiscalant solution similar to all other cases.

380

Figure 7. SEM micrographs showing the morphology of scale deposited on coupons for seawater with 1.5 & 2.5 CF at 70°C & 98°C at different concentrations of antiscalant

This change in the morphology of the crystals supports and reflects the crystal modification or alteration mechanism, as shown in figure 1. When antiscalant interferes the crystal growth phase, it either occupies the active growth site or blocks it to prevent further orderly arrangement to form a crystal. Therefore, it tends to deform the actual shape of the crystal leading to the deformed crystals. The addition of antiscalant doesn't allow to grow the crystal in a uniform pattern, and distorted morphology was created, which is round-shaped in this study. Therefore, the crystal formed in the presence of the antiscalant were observed to be of round shaped. This change in morphology of the crystals doesn't allow the crystals to adhere to the surface firmly as pure crystal. Hence, crystals were observed to be deposited in a scattered fashion.

For seawater with higher CF and temperature, the concentration of antiscalant is very crucial. At 1 ppm concentration of antiscalant, it is inferred that this dose was not enough to prevent the aggregation of calcium and sulfate ions and needle-shaped crystals of calcium sulfate were deposited. But at this concentration, antiscalant managed to occupy the space lattice in CaCO_3 crystal formation and resulted in the round /sphere shaped crystals. On the other hand, for the seawater with 2 ppm of antiscalant, the concentration of antiscalant was enough to act as threshold barrier to prevent sulfate crystal formation but participated in deforming CaCO_3 crystals to round-shaped and also resulted in a substantial increase in the turbidity of the solution as depicted in figure 6(b).

4. Conclusions

This work displays the inhibition mechanism of the tetra polymer-based antiscalant on the seawater with a CF of 1.5 and 2.5 with assorted dosages of antiscalant. It was observed that there were changes in the solution chemistry, altering the value of pH, alkalinity as a result of various chemical equilibrium shifts due to heating. Addition of antiscalant delayed the scaling, and it elucidated the inhibitory mechanism as a threshold barrier to prevent the ions to aggregate. It was found to accelerate the decomposition of HCO_3^- ions further to produce more hydroxyl ions to prevent carbonate scale formation. Hence, the retention time for seawater increased at a higher temperature without scaling, and it was observed to be proportional to the concentration of antiscalant. However, the threshold barrier mechanism was observed to be dependent on CF of seawater, the dosage of antiscalant maintained, and temperature. A higher dose of antiscalant was required to inhibit the scale formation for the relatively higher concentration of seawater and at a higher temperature. Form morphological studies, It was observed that the addition of tetrapolymer antiscalant distorted the regular shapes of the carbonate crystals depicting the scale preventing mode of crystal modification mechanism. It resulted in round/sphere-shaped crystals. Thus, the inhibitory action of tetrapolymer based antiscalant was a cumulative effect of the dual mechanisms involving threshold inhibition and crystal distortion.

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428

429 **Nomenclature**

430 CF- Concentration Factor

431 PA- Phenolphthalein Alkalinity

432 TA- Total Alkalinity

433 ppm- parts per million

434 CaCO_3 - Calcium Carbonate435 HCO_3^- - Bicarbonate ions436 CO_3^{2-} - Carbonate ions

437 SEM- Scanning Electron Microscopy

438 EDAX - Energy Dispersive X-Ray Analysis

439 NTU- Nephelometric Turbidity Units

440

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