SCALE FORMATION IN THERMALLY-DRIVEN SEAWATER DESALINATION: EVALUATION OF TETRAPOLYMER ANTISCALANT AT HIGHER TEMPERATURE OPERATION

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ABSTRACT

Deposition of scales is quite common and prevalent in thermally driven desalination processes such as Multi-effect distillation (MED) and Multi-stage flash distillation (MSF). With temperature, various salts / ions (Ca²⁺, Mg²⁺, CO³⁻, SO₄²⁻ etc.) dissolved in the sea/brackish water, start precipitating and depositing; impeding the heat transfer necessary for evaporation. This limitation poses tremendous challenges; tends to restrict the efficiency and economics of thermal desalination. This study is about optimizing the dosage and scale inhibitory action of newly developed tetra polymer based antiscalant at 70°C and 98°C with Red Seawater at concentration factor (CF) of 1.5 and 2.5 with 1ppm, 2ppm and 4 ppm dosing (as product) of antiscalant under reflux condition for seven days along with metallic coupons. To understand the role of antiscalant and onset of scale deposition, the inhibition action was evaluated by monitoring pH, turbidity, and alkalinity. It was observed that addition of antiscalant displayed its inhibitory action by altering alkalinity resulting in either delay or completely suppressing the scale deposition depending upon dosage of antiscalant. It was also learnt that scale deposition and inhibition were closely related to changes in pH and alkalinity which were also reflected in turbidity measurements. Scales deposited on the coupons were also analyzed for morphology and constituent elements by SEM/EDAX which further supported the inhibitory action of newly developed tetrapolymer antiscalant at a dose of ~2-4 ppm depending upon seawater CF and temperature.

Keywords: Scales, Thermal Desalination, Antiscalant, Alkalinity

1 INTRODUCTION

The deposition of the scales in water related industries is widely anticipated issue. This is one of the major problem faced by most of the seawater distillation plants. Most of the scales deposited are from the sparingly soluble ions present in water viz. calcium, magnesium, carbonate, sulfate, silica etc. Scaling happens when these sparingly soluble ions are concentrated beyond their solubility limits (Stumm, 1995, Hamrouni and Dhaibi, 2001, Amjad, 2015) either by water evaporation (cooling tower, MED, MSF, MD)(Shams El Din et al., 2005, El-Dessouky et al., 2004, Hillier, 1952, Hoang, 2015, Langelier, 1954, Mubarak, 1998, Schwarz and Bart, 2016) or by water separation (SWRO)(Antony et al., 2011). The deposition of scales can cost the efficiency of the desalination process (Schwarzer and Bart, 2016) by loss of heat transfer occurring on the surface in thermally driven processes or by decline in the permeation through membranes (Antony et al., 2011). As a consequence of scaling, the top brine temperature (TBT) in thermal desalination processes is restricted to 70°C, especially in multi-effect distillation and membrane distillation. Most of the scales deposited in thermal processes are of calcium carbonate and magnesium hydroxide but it can also lead to deposition of harder scales of calcium sulfate if temperature
and concentration of seawater are increased further (Alahmad, 2008, Dooly and Glater, 1972, El Din et al., 2005, Fellows and Al-Hamzah, 2015, Shams El Din et al., 2005).

There are various theories and mechanisms reported about scale formation in seawater and about their relation to pH, temperature and ionic strength of carbonic acid species (bicarbonate/carbonate ions, dissolved carbon dioxide) (Amjad, 2015, Amjad and Koutsoukos, 2014, Alahmad, 2008, Antony et al., 2011, Fellows and Al-Hamzah, 2015, Langelier, 1954, Rahman and Amjad, 2010, Shams El Din et al., 2005). According to Langelier (Langelier et al., 1950), scale formation starts with thermal decomposition of bicarbonate ions to produce carbonate ions as illustrated in eq. 1 and this combines with calcium to form calcium carbonate (eq. 2). This is followed by hydrolysis of carbonate ions (eq. 3) to generate hydroxide ions initiating magnesium hydroxide scale formation (eq. 4). In another theory, the thermal decomposition of bicarbonate first produces hydroxide ions (Dooly and Glater, 1972) which further results in the formation of carbonate ions as explained in equation 6.

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\begin{align*}
2\text{HCO}_3^- & \xrightarrow{\Delta} \text{CO}_3^{2-} + \text{CO}_2 \uparrow + \text{H}_2\text{O} & 1 \\
\text{Ca}^{2+} + \text{CO}_3^{2-} & \rightarrow \text{CaCO}_3 & 2 \\
\text{CO}_3^{2-} + \text{H}_2\text{O} & \xrightarrow{\Delta} \text{CO}_2 \uparrow + 2\text{OH}^- & 3 \\
\text{Mg}^{2+} + \text{OH}^- & \rightarrow \text{Mg(OH)}_2 & 4 \\
\text{HCO}_3^- & \xrightarrow{\Delta} \text{OH}^- + \text{CO}_2 \uparrow & 5 \\
\text{HCO}_3^- + \text{OH}^- & \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} & 6
\end{align*}
\]

There are also different models in literature which support carbonate scale formation mechanism at lower temperature (< 80°C) whereas at higher temperature these favor formation of magnesium hydroxide (García et al., 2006, Hasson et al., 1978, Mubarak, 1998, Pitzer, 1986, York and Schorle, 1966). Despite these all, it is still quite ambiguous about the mechanism for alkaline scale formation with respect to competitiveness towards either calcium carbonate or magnesium hydroxide (García et al., 2006, Hasson et al., 1978, Mubarak, 1998, Pitzer, 1986, Schwarzer and Bart, 2016, Shams El Din et al., 2002, Shams El Din et al., 2005, Shams El Din and Mohammed, 1988, York and Schorle, 1966).

To increase the TBT for thermal desalination, though different approaches have been exploited viz. acid addition, nano-filtration, thermal shock etc. (Abd-Eltwab et al., 2016, Al-Sofi et al., 1998, Ayoub et al., 2014, Chernozubov et al., 1966, Tabata, 1974) but the use of antiscalants seem most convenient and effective way to tackle scale formation. There are various reports and studies for the development and evaluation of ecofriendly, stable, efficient and economic antiscalants (Al-Rawajfeh et al., 2015, Budhiraja and Fares, 2008, Chauhan et al., 2012, Hamed et al., 1999, Hoang, 2015) and still lots of developments are going on in this regard. The main objective of this study is to evaluate the performance of newly developed tetrapolymer based antiscalant with real water (Red Seawater) at higher temperature range (up to 98°C) to prevent scale formation and to understand the mechanism of scale formation by monitoring pH, turbidity, and alkalinity. The morphological changes and elemental composition of the scales were also examined by using SEM/EDAX.

2 EXPERIMENTAL DETAILS

2.1 MATERIALS

Fresh Red seawater was used to perform the scaling experiment. Sea water was collected and concentrated under vacuum (20 mbar) at 30°C in rotatory evaporator. The concentration of seawater was maintained to 1.5 and 2.5 factor by measuring conductivity at room temperature and adding fresh Red seawater. The pH and turbidity of the experimental solutions were measured prior to each experiment.
Titration method was used to measure the alkalinity by adding phenolphthalein and mixed indicator (Bromocresol Green/Methyl Red). 0.002N HNO₃ solution was used as titrant. Stock solution of tetra polymer antiscalant (400 ppm) was prepared in distilled water. The scaling experiments were carried out with 400 ml seawater of mentioned concentration factors (CFs) at controlled temperature of 70°C and 90°C under reflux in three necked round bottle flask with stirring at 450rpm, using oil baths to maintain uniform temperature. The stock solution of antiscalant was added by maintaining volume to 400ml to obtain antiscalant dose of 0ppm, 1ppm, 2ppm and 4ppm. Small coupons were used to examine the scale deposition (figure 1) by Scanning Electron Microscope/ Energy Dispersive X-Ray Analysis (SEM/EDAX).

![Experimental set up for seawater scaling study](image)

2.2 METHODS

The aliquots were refluxed at assorted concentration and temperature with defined dose of antiscalant for seven days. The solutions were pipetted out immediate after experimental temperature was achieved and at defined time intervals. Immediate turbidity was measured followed by cooling down the solution at room temperature. Prior to measuring the pH and alkalinity of the samples, these were centrifuged at 9000 rpm for 10 minutes to settle down all the precipitates. 5ml of the supernatant was pipetted out into conical flask and titrated with 0.002 N HNO₃. The coupons were removed from the flask and dried for morphological and elemental analysis with SEM/EDAX.

3 RESULT DISCUSSION

The findings of the scaling experiments with assorted dose of tetra polymer based antiscalant at two different concentration factors of 1.5 & 2.5 and at two different temperatures of 70°C and 98°C with Red Seawater are presented and discussed in the following.
### 3.1 SCALE FORMATION AT 70°C

**Figure 2 Variation in pH, Alkalinity (Left plot) and Turbidity (Right Plot) for seawater with CF 1.5 at 70°C under reflux condition**

Figures 2 & 3 depict the effect of tetra polymer antiscalant on pH, alkalinity and turbidity at 70°C for seawater with concentration factor of 1.5 and 2.5 respectively. It was observed that the pH of baseline condition for both CFs started declining immediately after it reached 70°C followed by gradual increment again in pH value. Although, the change in the pH was quite substantial and faster (just after 10 hours) for seawater with 2.5 CF than with 1.5 CF. The initial drop in pH value is anticipated due to formation of calcium carbonate which aligns with Langelier theory (Langelier, 1954, Langelier et al., 1950) of bicarbonate decomposition as shown in equation 1 & 2. According to him, heating of the seawater results in thermal decomposition of bicarbonate ions shifting equation 1 in forward direction and results in formation of carbonate ions. As concentration of bicarbonate ions started declining with time, the decomposition of bicarbonate ions seemed to favor hydroxyl ions formation as explained in equations 5 & 6 (Dooly and Glater, 1972, Fellows and Al-Hamzah, 2015, Hoang, 2015, Langelier, 1954, Langelier et al., 1950), contributing towards gradual increment in pH value after initial decline and it was more intense in seawater with higher concentration.

It is quite evident from figures 2 & 3 that overall alkalinity of the seawater solution also declined with time. As most of the carbonic species (bicarbonate and carbonate ions) participated in scale formation, so it was reflected in the subsequent drop in alkalinity. As seen from the figures, turbidity values also increased immediately which was contemporaneous to decline in alkalinity for base line run and formation of crystals, though the value of turbidity was substantially higher for seawater with higher concentration. The immediate increase in the turbidity can be attributed to agglomeration and crystal formations which later induced nucleation on the surface of the round bottom flask and coupons, causing the deposition of crystals of CaCO₃ and their growth. The growth of the crystals initiated immediate decline in turbidity which started nearly after 2 hours of heating till it stabilized. At higher CF (2.5), turbidity for baseline was much higher due to higher concentration of carbonic species ions and it soared abruptly after 120 hours, which is suspected to be due to modification or weakening of carbonate scales by incorporation of magnesium hydroxide formed due to decomposition of carbonate ions into hydroxyl ions with time.
Addition of tetra polymer antiscalant seems to induce some physio-chemical changes affecting the scaling mechanism. As depicted in the figures 2 & 3, it was observed that pH of seawater with antiscalant seemed to resist any changes initially and then started increasing gradually followed by its sharp decline depending on the concentration of antiscalant. Similar trends were observed for change in alkalinity for seawater with antiscalant. It is believed that addition of antiscalant interfered in scale formation by shielding the calcium ions responsible for carbonate scales as expected from equation 1 & 2. This lead to further decomposition of bicarbonate and bicarbonate ions to form hydroxyl ion as explained earlier, contributing towards pH increase of the solution. Therefore, carbonate scale formation was delayed and this delay in scale formation was found to be related to the concentration of antiscalant as evident form the figures 2 & 3.

The increment in the pH continued till the concentration of hydroxyl ion exceeded solubility product of magnesium ion and hydroxide ions which subsequently initiated magnesium hydroxide scale formation. Formation of magnesium hydroxide scales further decreased the pH of solution due to removal of hydroxyl ion and hence, shifted the decomposition of the bicarbonate. This was also reflected in the turbidity of the solution. As soon as scale formation was initiated, turbidity of the seawater solution also started increasing. The change in turbidity was also found to be related to the concentration of antiscalant which governed scale formation. At low concentration of antiscalant, calcium carbonate was the major contributor in scale formation, hence the value of turbidity stabilized after certain time period due to deposition of the crystals. But at higher concentration of antiscalant, formation of hydroxides and antiscalant affinity towards calcium suppressed carbonate scale formation and lead to formation and
incorporation of magnesium hydroxide which were not adhered strong enough to the surface than calcium carbonate. Therefore, increase in the turbidity of the solutions observed due to dispersion of the scales.

The modification of the scales either by incorporation of magnesium or preference to from magnesium hydroxide was also supported by SEM/EDAX analysis from the crystals deposited on the coupons. Figures 4 & 5 depict the SEM/EDAX analysis of the scales deposited on the coupons at 70°C. It was observed that calcium (Ca) element was the major constituent of the scales formed without use of antiscalant, though traces of magnesium (Mg) element were also observed which was expected and reflected from pH and alkalinity analysis.

The extent of scale deposition on the coupons at lower concentration of seawater was dependent on the concentration of antiscalant as reflected in SEM micrographs in figure 4. It is clear from EDAX spectra that the use of tetra polymer antiscalant suppressed the participation of calcium (Ca) in scale formation and favored magnesium hydroxide scale formation along with silica which was quite surprising. Similarly, at higher concentration of seawater, most of the scales formed were from calcium carbonate with traces of magnesium for base line conditions as depicted in figure 5. Therefore, the use of antiscalant enhanced the incorporation of magnesium and silica as observed from SEM/EDAX analysis and nearly restricted calcium ions to participate in scale formation at higher dose (4ppm).

### 3.2 SCALE FORMATION AT 98°C

As discussed earlier, the composition and mechanism of the scale formation differ slightly at higher temperature (>80°C). At this temperature range, most of the bicarbonate ions thermally decompose to evolve carbon dioxide and hydroxide ion (Dooly and Glater, 1972). The scale formed at higher temperature are mostly made up of calcium sulfate which become prominent with higher seawater concentration. Figures 6-7 depict the inhibitory effect of tetra polymer based antiscalant reflected in the analysis of various parameters viz. pH, alkalinity and turbidity at 98°C which is further supported by the analysis of crystals/ deposits by SEM/EDAX technique for their compositional and morphological changes.
Figures 6 & 7 illustrate the effect of addition of tetra polymer antiscalant on the value of pH, turbidity and alkalinity with time at seawater concentration factor of 1.5 and 2.5 respectively. At lower seawater CF, it was observed that pH declined immediately after reaching the experimental temperature (98°C) which resulted in immediate decline in alkalinity followed by subsequent increase in turbidity. These changes were ascribed to calcium carbonate agglomeration favored by higher temperature. Meanwhile, carbonic species present in water started to dissociate to form hydroxyl ions and resulted in gradual increase of pH.

As explained earlier that formation of hydroxyl ions favored the formation of magnesium scales and at around 80 hours, the concentration of hydroxyl ions reached beyond solubility limit to induce precipitation of magnesium hydroxide scale. Therefore, the value of the turbidity also changed abruptly at the same time. As evident from the alkalinity analysis that the use of antiscalant inhibited calcium ions to combine with carbonate ions to form carbonic scales and hence slowed down the alkalinity drop. The pH of the solution was raised up slightly before transforming to hydroxyl scales as expected from decomposition of bicarbonates at higher temperature. It is quite evident form the figures 6&7 that the changes in the value of pH and delay in the decline in alkalinity were directly related to concentration of antiscalant. More the concentration of antiscalant, more it delayed/resisted the changes in pH, alkalinity and turbidity.

Similarly for higher concentration (2.5 CF) of seawater, deviations were more vigorous for alkalinity drop and pH which could be attributed to higher concentration of seawater. At this CF and temperature, it is believed that sulfate ions exceeded the solubility product for calcium sulfate scale formation. The pH of the solution also stabilized after initial abrupt fall because of counter effect of hydroxyl ion produced.
from the decomposition of carbonic species ions till hydroxyl ions concentration exceeded to the level to induce magnesium hydroxide scale formation. Addition of antiscalant again interacted in such a way to retain the pH and alkalinity of seawater depending upon the concentration of tetratpolymer antiscalant. Similarly, the value of turbidity (figures 6&7) observed for this concentration factors were exceptionally higher than seawater with 1.5 CF due to higher concentration of ions and their participation in scale formation.

Figure 8. SEM/EDAX micrographs showing the effect of antiscalant on morphological changes and elemental composition of the scales at 98°C on seawater with CF 1.5

Figure 9. SEM/EDAX micrographs showing the effect of antiscalant on morphological changes and elemental composition of the scales at 98°C on seawater with CF 2.5

SEM/EDAX analysis as depicted in figures 8 & 9 also support the formation of sulfate, magnesium and silica scales than carbonate at higher temperature. At lower concentration of seawater as depicted in figure 8, no traces of calcium were observed from EDAX analysis. At higher CF (2.5), calcium ions combined with sulfate ions to form calcium sulfate crystals along with magnesium hydroxide displaying prominent peaks of S and Ca elements and feeble peaks of Mg and Si for base line. But addition of the antiscalant suppressed the calcium participation in scale formation which was also supported by SEM micrographs and EDAX spectrum as discussed earlier during the analysis of pH and alkalinity variations. Therefore, the peak of calcium element faded with the concentration of antiscalant and peaks of magnesium and silica became more intense and prominent.
Figure 10 depicts the overall inhibitory effect of assorted concentrations of antiscalant on total reduction in scale formation by weight at different concentration of seawater and temperature. The amount of scale formed at 1.5CF of seawater reduced by ~75% at 4ppm dose of tetrapolymer antiscalant whereas it reduced to ~10% at 2.5 CF of seawater with same dose of antiscalant irrespective of the temperatures. Hence, the addition of tetrapolymer antiscalant effectively minimized the overall scale formation by restricting and shielding the calcium ions resulting in either delay or by shifting the equilibrium towards magnesium scale formation.

4 CONCLUSION

It is concluded that seawater concentration factor and temperature are very crucial and govern the scale formation. Monitoring the values of pH, alkalinity and turbidity are important; these can suggest the onset point of scale formation. Addition of newly developed tetrapolymer antiscalant is very effective in preventing calcium ions to participate in scales formation but it’s not efficient enough to prevent scales from magnesium and silica. It is also concluded that amount of antiscalant needed to prevent the scales is dependent on the duration of experiment or residence time for seawater while heating. Longer the residence time, more will be scale formation and higher dose of antiscalant will be needed. The optimum dose of tetrapolymer antiscalant needed is found to vary from 2-4 ppm which is directly related to seawater concentration (up to 2.5 CF), temperature and duration of experiment/residence time under reflux condition for seven days or less.

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REFERENCES


