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New anti-scalant performance evaluation for MSF technology

Amr Mohamed[a,*], Justin Robert[a], Abdel Nasser Mabrouk[a], Imteyaz Ahmad[a], Ahmed Nafey[a], J.S. Choi[a], J.K. Park[a], Stephan Nied[b], Jurgen Detering[b]

[a]*Doosan Water R&D Center, Monarch Office Tower, Level 29th, Sh. Zayed Road, Dubai, UAE*
Tel. +971 509758938; email: Amr.Elrefaay@doosan.com
[b]*BASF SE, Care Chemicals & Formulators, D-67056 Ludwigshafen, Germany*

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ABSTRACT

The desalination industries are looking for the reduction in the unit cost of desalinated water through developments in the technologies, process optimization, etc.; multi stage flash (MSF) technology has a proven track record for high reliability in the tough seawater condition. One of the technical barriers to improve the MSF system performance is the scale formation phenomena. This phenomenon can be manipulated by nanofiltration or by chemical treatment (anti-scalant). A pilot plant was constructed to evaluate the performance of a novel anti-scalant, under high top brine temperature (TBT) condition. Techniques such as atomic absorption spectroscopy and X-ray diffraction are used to measure the scale deposition in the test sections. Different operation parameters such as TBT, salinity, dosing rate, and operation with/without ball cleaning are considered. The experimental results indicate that the scale inhibition shows good performance after 72 h even for a low dosing rate of 2.5 ppm.

Keywords: Multi stage flash; Anti-scalant; Top brine temperature; Scale formation

1. Introduction

Doosan Heavy Industries & Construction is a world leader in building large-scale desalination plants by multi stage flash (MSF), multiple-effect desalination, and reverse osmosis (RO) process as per the market needs. Consistent R&D effort has been performed by Doosan to maintain the market lead and to meet the increasing demand. MSF desalination process is considered to be the most reliable and mature technology for producing high-quality desalinated water on large-scale production for harsh seawater conditions persisting in Middle East. The reliability of MSF desalination process has motivated Doosan to increase the unit production capacity of the MSF plant as shown in Fig. 1. Further in the process of increasing the unit production capacity and reducing the specific water production cost, Doosan is focusing on developing large-scale MSF plants with increased efficiency.

One of the main parameters which is always an obstacle in scale-up of unit capacity of MSF desalination process is top brine temperature (TBT). Increasing the TBT will result in scale deposit inside the tubes, and this will affect plant performance in turn the water cost. The presence of scale in the tube will increase the fouling factor, which leads to reduction in overall heat transfer coefficient. This will result in increased heat transfer area which directly affects the CAPEX. On the other hand, the presence of scale in the tube will increase the pressure drop in turn the pumping power,

*Corresponding author.

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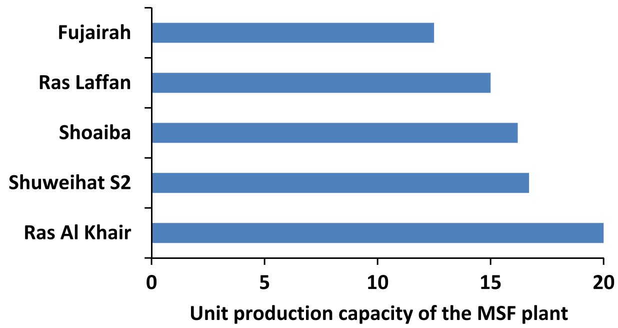

Fig. 1. Doosan MSF desalination plant unit capacity evolution.

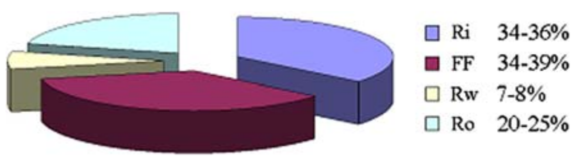

Fig. 2. Heat transfer resistances in MSF condenser.

the frequency of ball cleaning, and the chemicals dosing rate and steam consumption, which will lead to increase in OPEX. Fig. 2 shows typical heat transfer resistances in an MSF condenser which consist of inner (R_i) and outer (R_o) thermal resistances, wall thermal resistance (R_w), and fouling (FF) water, and it is very clear that fouling factor is the key element to enhance overall heat transfer coefficient.

Scale deposition in MSF consists of two types of scale: hard scale and soft scale. The soft scale formed from $CaCO_3$ which is amorphous and can be removed using sponge ball cleaning. The hard scale is mainly calcium sulfate resulted from the direct crystallization due to supersaturation of anhydrite ($CaSO_4$), hemihydrate ($CaSO_4 \cdot 1/2H_2O$), or gypsum ($CaSO_4 \cdot 2H_2O$). Most of the scale deposition is in the form of hemihydrate [1] as shown in Fig. 3.

Skillman et al. [2] developed a simple sulfate solubility index for estimating the likelihood of calcium sulfate scaling. Skillman index is a ratio between the actual concentration, $[i]_{\text{actual}}$, of either calcium or sulfate and its theoretical or equilibrium concentration whichever is the limiting species.

$$\text{Skillman index} = \frac{[i]_{\text{actual}}}{(\sqrt{x^2 + 4K_{SP}} - x)\cdot 10^3}$$

where x is the absolute value of the excess common ion concentration of calcium and sulfate ions:

$$x = |2.5[C^{2+}] - 1.04[SO_4^{2-}]|\cdot 10^{-5}$$

According to Linke et al. [3], the solubility product constant (K_{SP}) can be calculated as follows:

$$S = 2.91 + 0.003173T - 8.193\times 10^{-5}\times T^2$$

Several attempts have been made in the past to increase the TBT of MSF desalination process, and some of them are highlighted here. Al-Shammiri et al. [4] reported that the nanofiltration inhibits $CaSO_4$ scaling by 99.1–96.98% according to recovery ratio without adding any chemicals, nanofiltration has low prevention for $CaCO_3$ (5.3–23%), and also for all other scaling salts, a great scaling inhibition was found about 97.7% for $BaSO_4$, 99.8% for $SrSO_4$ scaling, and 94.86% inhibition for CaF. The reliability of this nano-

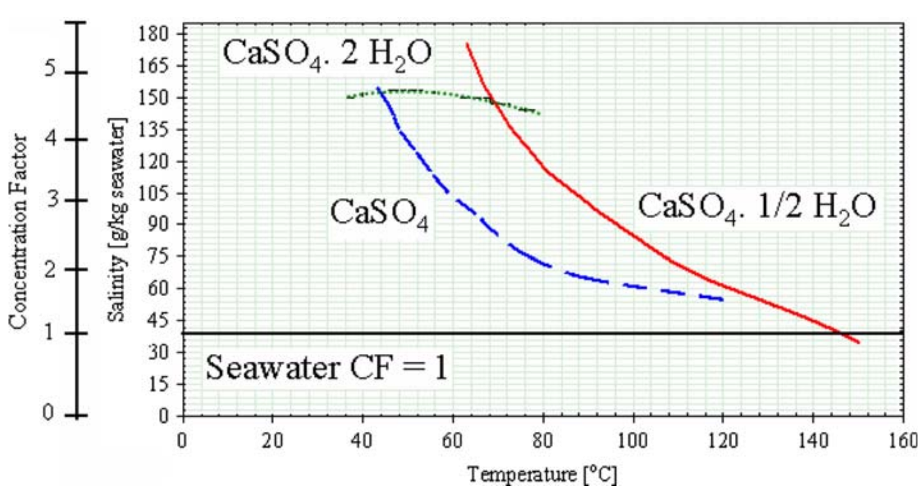

Fig. 3. Phase diagram of $CaSO_4$.

filtration system is tested in gulf seawater and found to be satisfactory.

The Saline Water Research Institute, Saudi Arabia (SWDRI), handled the problem of increasing the TBT with dihybrid nanofiltration (NF)/MSF and trihybrid NF/RO/MSF [5]. The experimental results of dihybrid system NF/MSF showed the excellent performance of nanofiltration process to remove the divalent ions, and even it is experimentally verified up to a TBT = 128˚C in their pilot plant. Such system can be worked safely through the use of a MSF makeup formed of a blend of NFP (nanofiltration permeate) and seawater in the ratio of 1:2 and 1:1 up to 130˚C. The test results on the trihybrid NF/RO/MSF configuration showed that it was possible to operate the MSF pilot plant with a makeup which was entirely formed of the reject of the reverse osmosis unit, operated in the NF/SWRO mode, up to 130˚C of TBT. It can also be operated with a makeup formed of a blend of brine reject of the RO unit and seawater in the ratio 2:1 and 1:1 safely up to a TBT of 128 and 122 ˚C, respectively.

The last three decades have witnessed serious efforts by developers of chemicals attempting to increase the top brine temperature where effectiveness of chemicals used in suppressing formation and deposition can be prolonged. Inhibition of scale formation is achieved by one of the following treatment methods [6]:

Use of acid causes depletion of carbonate present in seawater, this is known as acid treatment method.

Use of commercially available scale inhibitor.

Combined use of the above two, that is, use of scale inhibitors at reduced dosing rate with partial depletion of carbonate by acid, this is known as hybrid treatment method [7].

The commercially available anti-scalants are performing safely up to 112˚C in BR-MSF plants, and they are working well up to 118˚C in OT-MSF plants [8]. Only few published work is found in the area of MSF operating at TBT higher than 112˚C. Hamed el al. [6] conducted experiments with different scale commercially available inhibitors up to 119˚C of TBT using the MSF pilot plant available at SWDRI. The experiments are conducted for a period of one month for a dose rate of 1 ppm and the concentration factor of 1.9. The results showed positive indication for the possibility to increase the TBT with anti-scalant.

A techno-economical study [9] was performed by DOOSAN R&D center for OT-MSF configuration where the concentration factor equals to 1 instead of 1.4 in brine recycle mode. Increase in TBT will increase flash range, and the unit water production cost is decreased. Also, the study made with BR-MSF system at increased TBT up to 120˚C has resulted in decreased unit water production cost. This higher temperature operation is possible only if a new reliable anti-scalant is developed. In the above contest, DOOSAN made a collaborative R&D work with BASF, Germany, to develop a new anti-scalant.

Fig. 4. Experimental setup to study the scale deposit.

2. Experimental setup

To prove the reliability of the new anti-scalant at high TBT (between 120 and 130˚C), an experimental setup was developed in Changwon, South Korea. The experimental setup was designed in such a way that it simulates the real operating condition inside the MSF condenser tubes to study the scale deposits at different operating conditions. It consists of concentric tubular heat exchanger (40 tubes) inner tube diameter (OD) 20 and 50 mm outer tube diameter. It has the facility to collect scale deposits in the heated seawater through a coupon (metal chip) and tube section for both with and without ball cleaning. The reverse osmosis system in the pilot plant helps in achieving the gulf seawater condition by concentrating the incoming Korean seawater (33 g/l). It also has the provision to test the scale deposit on the test sample piece with ball cleaning mode of operation. Fig. 4 shows the experimental setup to study the scale deposit in the MSF plant.

3. Experimental plan

Sets of experiments (with and without ball cleaning) were conducted to investigate the performance of the new anti-scalant at TBT of 120, 125, and 130˚C for a varying seawater salinity of 50 and 65 g/l (corresponding to OT-MSF and BR-MSF conditions). The dosing rate was varied between 2.5 and 10 ppm (2.5, 4, 6, 8, and 10) for 24 h of continuous operation. Since the experiments are focused toward the anti-scalant performance against scale formation, the entire planned tests are conducted with titanium tubes and stainless tubes with and without ball cleaning operation.

4. Results and analysis

Visual inspection and chemical analysis were performed for the test samples to evaluate anti-scaling performance. The visual check gives a qualitative idea on the extent of scale deposits and the anti-scalant performance. Chemical analysis by the BASF lab indicates that calcium and magnesium are the major content in the scale; the others were neglected from the analysis. This analysis was performed by atomic absorption spectroscopy (AAS) in the units of g/m^2 of tube area.

Fig. 5. Coupon and tube samples—without ball cleaning.

Fig. 6. Coupon and tube samples—with ball cleaning.

Also the scanning electron microscope (SEM) was used to understand the microstructure of the scale.

Figs. 5 and 6 are photographs of the coupon sample during visual inspection. This gives a qualitative measure on the anti-scalant performance and the extent of scale deposits, before doing the chemical analysis.

From Figs. 5 and 6, it is understood that the scale deposit is less, when the experiments are conducted with ball cleaning comparing with the experiments without ball cleaning. Similar trend is seen for all the conducted experiments irrespective of the TBT, salinity, and dosing rate.

The SEM was used to understand the microstructure of the scale. The result obtained from SEM for a particular experiment conducted without ball cleaning system at TBT = 120°C, salinity 60 g/l, and dosing rate = 2.5 ppm is presented in Fig. 7.

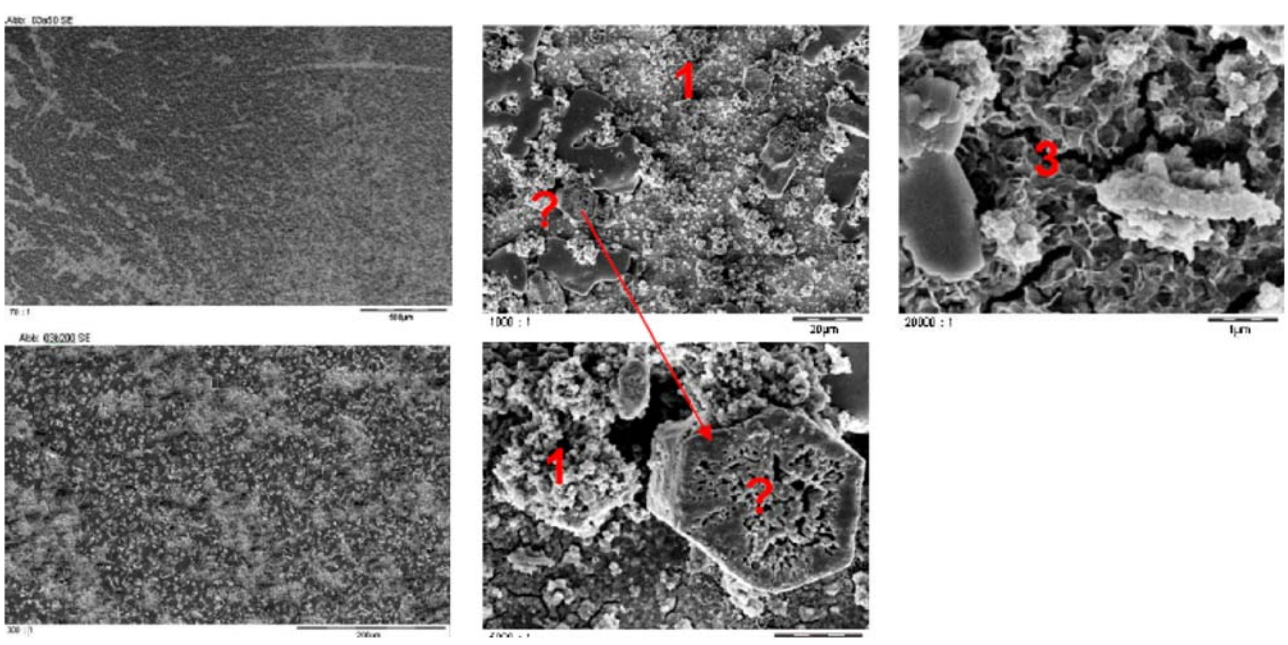

Fig. 7. SEM result at TBT = 120°C, salinity 60 g/l, and dosing rate = 2.5 ppm.

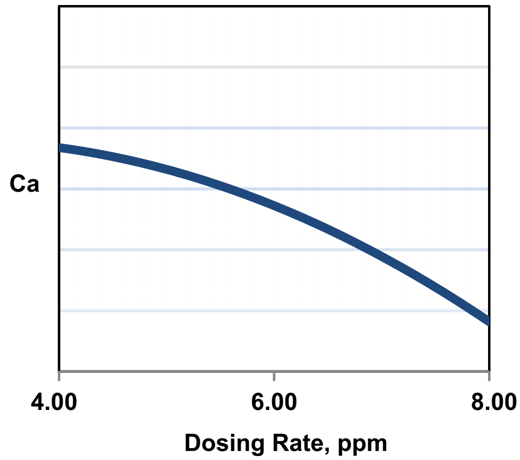

Fig. 8. Ca participation at TBT = 125℃ and salinity = 50 g/l.

From the SEM image, it is understood that the coupon surface is covered with an amorphous (1) and crystalline precipitation, Mg(OH)2-Crytals3 shaped sand rose (3). This precipitation is easily removable.

The calcium and magnesium in the scale deposit are estimated by AAS, and the same is represented in Figs. 8 and 9, corresponding to a test condition of TBT = 125℃ and salinity = 50 g/l without ball cleaning system in operation. Ca and Mg participation is represented in gram per unit area (g/m^2).

From the analysis, it is understood that the calcium and magnesium deposits reduce with an increase in anti-scalant dosing rate. Similar trend is seen in all the experiments. Also the precipitation is low, when the plant is operated with ball cleaning system.

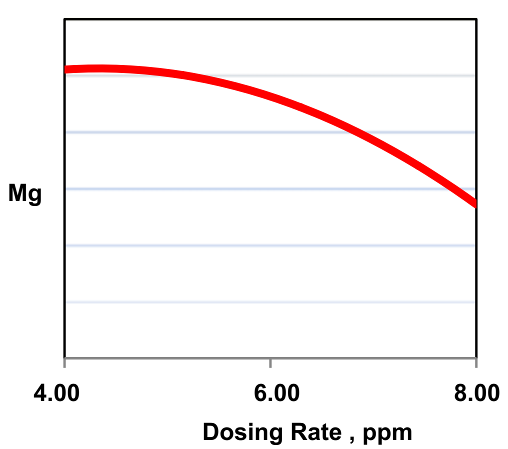

Fig. 9. Mg participation at TBT = 125℃ and salinity = 50 g/l.

5. Fouling factor evaluation

In order to calculate the fouling factor, the scale thickness needs to be calculated first and then the corresponding fouling factor is calculated. The following assumptions are made to simplify the calculations.

5.1. Assumptions

- Ca and Mg scales are in layers.
- The scales are in homogenous distribution.
- High-density scales (Ca) stick at the bottom layer (i.e. at the tube surface), and the lighter-density scale (Mg) sticks above the Ca.

Base on the above assumptions and the fundamentals of heat transfer, the following set of formulas were derived and these equations are used to calculate the thickness of the scale and in turn the thermal resistance by the scale (Fig. 10).

(1) Ca scale voulme (V_{Ca})

$$= \frac{\text{Ca scale } \frac{\mathrm{g}}{\mathrm{m}^2} \times \text{Tube surface area}}{\text{Ca density } \left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right) \times \frac{1000\ \mathrm{g}}{\mathrm{kg}}} (\mathrm{m}^3)$$

(2) Mg scale volume (V_{Mg})

$$= \frac{\text{Mg scale } \frac{\mathrm{g}}{\mathrm{m}^2} \times \text{Tube surface area}}{\text{Mg density } \left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right) \times \frac{1000\ \mathrm{g}}{\mathrm{kg}}} (\mathrm{m}^3)$$

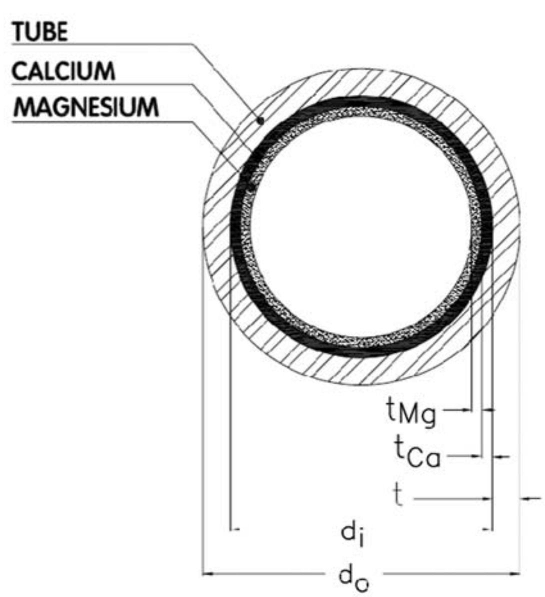

Fig. 10. Schematic diagram inside the scaled tubes.

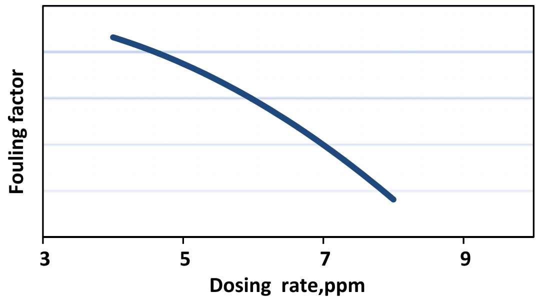

Fig. 11. Fouling factor at 50 g/l salinity without ball cleaning.

(3) Scale thickness (mm)

$$= \left[\frac{d_i \pm \sqrt{d_i^2 - \frac{4}{\pi l} \cdot V_{Ca}}}{2}\right]_{Ca} + \left[\frac{(d_i - 2t_{Ca}) \pm \sqrt{(d_i - 2t_{Ca})^2 - \frac{4}{\pi l} \cdot V_{Mg}}}{2}\right]_{Mg}$$

(4) Fouling factor $\left(m^2 \cdot \frac{C}{W}\right)$

$$= \left[\frac{\ln\left(\frac{d_i}{d_i - 2 \times t_{Ca}}\right)}{2\pi kl}\right]_{Ca} + \left[\frac{\ln\left(\frac{d_i - 2 \cdot t_{Ca}}{d_i - 2 \times (t_{Ca} + t_{Mg})}\right)}{2\pi kl}\right]_{Mg}$$

where d_o, tube outer diameter; d_i, tube inner diameter; t, tube thickness; l, tube length; t_{Mg}, magnesium scale thickness; t_{Ca}, calcium scale thickness.

From AAS results, the Ca scale is mainly formed from $CaCO_3$ and magnesium is present as $Mg(OH)_2$. The following property values are used in the above set of equations while calculating the fouling factor.

- Density of $Mg(OH)_2$ is 2,344 kg/m^3.
- Density of $CaCO_3$ is 2,710 kg/m^3.
- Thermal conductivity of $Mg(OH)_2$ is 8 $W\,m^{-1}\,K^{-1}$.
- Thermal conductivity of $CaCO_3$ is 2.2 $W\,m^{-1}\,K^{-1}$.

The fouling factor value based on the above equations is presented in Fig. 11 corresponding to 50 g/l salinity without ball cleaning.

The performance of the new anti-scalant is promising for 24- and 72-h operation, and long-time experimental operation (10 days test) is under processing.

6. Conclusion

To study the performance of a new anti-scalant at higher TBT corresponding to a once through and brine recycling configurations of MSF desalination system, an experimental setup was constructed in Changwon, Korea. Several experiments are conducted for a set of operating conditions. It is understood from the experiments that the scale deposit is less, with ball cleaning system compared to without ball cleaning. Similar trend is seen for all the conducted experiments irrespective of the TBT, salinity, and dosing rate. The scale precipitate obtained in the experiments is easy to remove (amorphous) by ball cleaning. The performance of the new anti-scalant is promising for 24- and 72-h operation, and long-time experimental operation (10 days test) is under processing.

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