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A bench-scale evaluation of scale inhibitors in multistage flash evaporation plants under high-temperature operation mode

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ABSTRACT

Seawater desalination is currently considered a vital and dependable water resource to meet all requirements of fresh water. Kuwait has been a leading country in fresh water production from the sea using the multistage flash (MSF) unit. All MSF plants in Kuwait are operated on the principle of chemical additives dosing for scale inhibition, and at a top brine temperature below 120˚C. This is because calcium sulfate scaling phenomenon usually occurs when the temperature is higher than 120˚C. This type of scaling is a hard scale that cannot be removed easily by chemical or mechanical cleaning. Until recent years, no antiscalants could overcome this type of scaling at high temperatures. The new generation of antiscalants is able to stand high operation temperature without hydrolysis or without losing their reactivity and can solve sulfate scaling problem. This paper consists of laboratory tests to evaluate the performance of new inhibitors that can overcome sulfate scaling. In particular, experiments were conducted to study the antiscalants effectiveness under different operating conditions with different brine concentration, especially in high-temperature operation mode. The result of the experiment showed that the performance of these chemical additives varied with the operating temperature, flow rate, and the brine concentration. The tested chemicals showed reduction in the percentage precipitation at high temperature up to 160˚C. A techno-economic feasibility study was also conducted.

Keywords: Seawater desalination; Brine water; Calcium carbonate; Calcium sulfate

1. Introduction

As a result of increasing population and due to limited water resources, Kuwait has adopted the distillation process in producing fresh water. Five multistage flash (MSF) desalination plants were built and operated during the last four decades. During this long period of time, Kuwait has gained valuable experience in design, operation, and maintenance of MSF desalination plants. However, the MSF plants suffer from serious problems such as corrosion, scaling, noncondensable gases, low-performance ratio, pressure losses through demisters and condensers, limited flash range, and very low productivity [1]. Scaling is the main problem which thermal desalination technologies face in producing fresh water. As a result of this phenomenon, Kuwait annually spends millions of US dollars to maintain and replace damaged sections of the MSF units [2].

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Scale is defined as a hard crystalline deposit, mainly consisting of inorganic salts, which adhere to heat transfer surfaces and require physical and/or chemical methods for their removal [3]. As scale is formed under operation condition, it could lead to a serious reduction of heat transfer coefficient and deposition of hard salts on the desalination equipment such as tubes, pipes, brine heater, demisters, heat exchanger, and other parts. For example, some heat transfer tubes and demisters mounted in Kuwait MSF units have been completely blocked by a hard crystalline scale [4]. Even if a thinner scale layer forms on the inner surface of the heat transfer area, it can lead to a considerable reduction in heat transfer and impose severe penalties on the thermal and economical efficiency of distillation plants.

There are two main types of scaling in desalination plants: alkaline and nonalkaline scaling (calcium sulfate scale). The alkaline scale consists primarily of calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$) or a mixture of both compounds which crystallize on heat transfer surfaces in contact with natural waters or brines [5]. Calcium sulfate scaling can exist in six crystalline forms, but only three forms can exist in contact with solutions. The three forms are anhydrite ($CaSO_4$), hemihydrate ($CaSO_4 \cdot 1/2H_2O$), and dihydrate (gypsum) ($CaSO_4 \cdot 2H_2O$). All these forms of calcium sulfate are more soluble than $CaCO_3$ and $Mg(OH)_2$, and form when the seawater is supersaturated with respect to calcium sulfate.

2. Scale inhibitor (additives)

Additives may act to shift crystalline scale formation by one of several possible routes. They may change the precipitation salts chemical potential by affecting complex formation and adsorption of precipitated ions on the scaling surface. Additives may also form a film on the metal surface, thus eliminating potential sites for adherence. They may adsorb onto the precipitating ions, thus inhibiting scale nucleation, or they may adsorb onto the growing crystals, thus distorting or inhibiting further crystal formation. The threshold inhibition is time related, where a threshold inhibitor can retard crystallization for a sufficiently long period of time so that the super saturation solution is removed from the system before that retardation time exceeds.

In the commercial market, there are many different types of polyelectrolyte scaling inhibitors, which are blends of more than one type of polymer, and are sold under different brand names. For example, Calgon El-2438 is an alkaline scale inhibitor that consists of polycarboxylate and phosphonate. However, Calgon SHMP is sodium hexametaphosphate [6]. This product was applied successfully at a dosage level of 6 mg/l for three years at the Al-Jubail plant in Saudi Arabia [7].

EV2000, EV2030, EV2035, EV2050, EV, and EVN are all different types of Belgard antiscalant, which is a product of Ciba Geigy before and currently product of B-water additives (BWA) company. Belgard EV2030 is a neutralized enhanced carboxylic polymer. This product was introduced in the market during the 1973s as a cost-effective additive for low-temperature application. Field testing of Belgard EV2000, EV2030, and EV2035 at many locations was successful. Therefore, it is now being used throughout the Middle East in plants operating at top brine temperature of 80–105℃ and dosage levels of 0.6–3.0 mg/l [8].

Another laboratory test was done at 60℃ to test the performance of different types of maleates antiscalant. Result showed that maleates (EM-1 Belgard EV 2050) is a polycarboxylic acid-based polymer, and has superior multifunction properties compared to the others. EM-1 showed inhibition in percentage for Mg $(OH)_2$ up to 90%, while it can control calcium sulfate up to 50%, and also control $CaCO_3$ deposition up to 60% inhibition [9].

There are also other different types of antiscalants available in the desalination markets, as 1-hydroxyethylideene1–1 diphoshonic acid (HEDP), amino trimethylene phosphonic acid (AMP), hexamelhylene diamine tetra melthylene phosphonic acid (HDMTMP), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA), a copoly mer of acrylic acid and 2-acrylamino-2-methylpropyl sulfonic acid (AA/AMPS), poly amino polyether methylene phosphonic acid (PAPEMP), poly maleic acid (PMA) such as Sokalan PM101, and Phosphonate as Albrivap DSB and Aquamax LT-19.

PAPEMP is considered one of the new advanced antiscalants. Their performance in preventing $CaCO_3$ scaling was evaluated using calcite saturation solution. The result showed that at a dosing of 25 mg/l of PAPEMP, $CaCO_3$ scaling can be inhibited up to 100% at 55℃, while other chemicals as polyacrylic acid prevents only up to 53% $CaCO_3$ at the same temperature. Other antiscalants as HEDP can only prevent $CaCO_3$ scaling up to 38% even though a 25 mg/l dosing of antiscalants have been used. PAPEMP also showed a 100% inhibition for calcium sulfate scaling at 65℃ with a dosing rate of 0.5, while about 28 mg/l of sodium hexametaphosphate (SHMP) is required to reach the same inhibition percentage of calcium sulfate at the same operating conditions [10].

Kuwait MSF plants used the Hagevap product (polyphosphate-based treatment) starting from 1955 at dosage rate of 4.0 mg/l and a top brine temperature of 90°C. A polyphosphate blend (Shuwaikh mixture) was then developed by the Ministry of Electricity and Water (49% sodium-polyphosphate, 49% lignin sulfonate, and 2% anti-foam). This product was found to be cost effective and efficient at dosage levels of 4–5 mg/l at top brine temperature of 90°C. Kuwait MSF plants are normally designed to meet water projected many years ahead and can satisfy present water demand readily by operation at low temperature when polyphosphate-based treatments are successfully applied. However, as water demand escalates and the operating economy becomes increasingly important, a move towards high-temperature operation and use of antiscalants can be anticipated.

Some of these antiscalants, like Belgard EVN, were tested in 1977 and continued being used till 1983 with the 4,546 m^3/d MSF unit of Shuwaikh at low temperature, and was found to be effective at a dosage level of 2.0 mg/l.

Other commercial antiscalants were also tested and proved effective up to a temperature of 93°C, however, their unit price made them uneconomical. In 1982, a Belgard EVN and Shuwaikh mixture were tested in two similar capacity units for one year. The trial revealed that, despite the high unit price of Belgard EVN, it was more effective compared with polyphosphate treatment. Furthermore, the need of acid treatment was less, which means less corrosion and longer unit life.

A summary of the chemicals used for scale control in some of the GCC countries are presented in Table 1 and a comparison between the acid and polyphosphate additives is presented in Table 2.

All the evaluated antiscalants were evaluated at low operating temperature, and there was no such evaluation carried out at a temperature greater than 120°C, and most of the antiscalants which, are effective in controlling alkaline scale at low temperatures, were found ineffective at higher temperatures. Although a variety of chemicals are used in the Arabian Gulf MSF plants in general, each antiscalant is used at different operation conditions at top brine temperature, brine concentration, and dosing rate. For this reason, it is difficult to compare their technical availability. This problem was solved through an evaluation of different types of antiscalants at the same operation condition in this current study. In particular, the work was focused on the potential of these antiscalants in preventing or minimizing scale formation at high operating temperature in Kuwait MSF plants, and a techno-economic feasibility study was also conducted.

3. Testing technique

This bench-scale study was conducted to evaluate the technical reliability of a new generation of commercially available high-temperature antiscalants for MSF distillation to avoid all scaling problems. The instrument used in the test was OP-Mack 2500 device (Fig. 1), which is designed to provide evaluations of scale inhibitors under dynamic conditions by mimicking the conditions under which the scale is deposited in the MSF plants. The scale is deposited giving $CaCO_3$, $Mg(OH)_2$, and calcium sulfate scaling. The type of precipitated scaling was specified by chemical analysis and pressure drops across capillary test tubes.

First, the brine solution was filtered using 0.45 μm to ensure that all the particulate matter, which may act as nucleation sites are removed. Then the brine water was pumped through the system using high-pressure liquid chromatography (HPLC) pumps, capable of delivering a constant flow rate according to the experiments conditions. HPLC pumps can supply a solution with a different flow varying from 1 to 100 ml/min, and the system can be operated under a back pressure of 20–50 psi.

The brine water was then heated inside the oven to a desired temperature under controlled back pressure, where the effect of high temperature on the inhibitor performance can be evaluated without losing the water through evaporation. The temperature inside the oven can be controlled using a displayed controller to set the temperature from 90 up to 180°C.

The heated brine was then circulated through a capillary test tube (Fig. 1), and the scale formation rate was checked through measurements of soluble calcium, sulfate, magnesium, and bicarbonate concentration, then compared to the initial concentration in the brine solution.

The tested solution was withdrawn every 15 min for analysis. The bicarbonate ion was determined using an Environmental Protection Agency (EPA) approved acid titration method. The calcium and magnesium ions in the tested solution were analyzed using titration method with a 0.2 N ethylenediamine-tetraacetic acid (EDTA) titrant, while sulfate was determined by spectrophotometer from Hach (DRL/2000). The differences between the final ion concentration and the total ion present initially in the solution over the initial ion concentration in the tested solution represent the percentage precipitate.

Table 1
Methods of scale control used in some commercial MSF plants located in the Arabian Gulf Region

Plant location	Total capacity (m^3/d)	Total No. of units	Design TBT[a] (℃)	Design scale additive (ppm)	Trial TBT (℃)	Trial scale additive (ppm)	Current treatment
Kuwait							
(1) Shuwaikh	127,288	7	90	Polyphosphate-based shuwaikh mixture			Shuwaikh mixture or Belgard EVN
(2) Shuwaikh F	9,092	2	88	As above	93 93 93	Darex 40 (1.4–6) Calonx 214 Vaptreat H	As above
(3) Shuaiba North	40,914	4	89	Shuwaikh- mixture (3.5–5)	105	Belgard EVN 2	As above
(4) Shuaiba South	136,380	6	89–90	As above			As above
(5) Doha East	190,932	7	90	As above			
(6) Doha East A8	4,546	1	121–138	Acid	NA[b]	NA	NA
(7) Doha West	4,366,416	16	91–110	Shuwaikh mixture			Shuwaikh mixture or Belgard EVN
(8) Al Zour	218,208	8	90	Shuwaikh mixture	105		As above
Saudi Arabia							
(1) Jeddah	22,730	2	121.1	H_2SO_4 Antifoam		H_2SO_4 Antifoam	H_2SO_4 & Antifoam
(2) South East of the Arabian Peninsula	27,276	16	105–112	NA[b]	110	Nalco 8,599 -NA (7)	Nalco 8,599 Nalco 8,599
(3) Yanbu	19,200	2	110	HTA[c]	110	Calgon El-2438	Calgon El-2438
(4) Ghazian	10,000	3	112.8	Acid	107.2	Albrivap G Albrivap DSB & Acid	Hybrid treatment acid, Albrivap DSB)
(5) Al Jaball phase I	136,380	6	90.6	Polyphosphate based	90.6	Belgard EVN 5 Albrivap—B 3 Flocon 247 3 Albrivap A 5 Shuwaikh mixture 4.2	As above

(*Continued*)

Table 1 (*continued*)

Plant location	Total capacity (m^3/d)	Total No. of units	Design TBT[a] (°C)	Design scale additive (ppm)	Trial TBT (°C)	Trial scale additive (ppm)	Current treatment
Al Jaball phase II	940,000	40	90.6/112.8	Polyphosphate-based (4)/ HTA[c]	NA	NA	NA
Qatar							
Ras Abu Fontas phase I	18,184/22,730	2	91/112	Polyphosphate-based/ Belgrad	105–110	Belgrad EV	Belgrad EV
Ras Abu Fontas phase II	As above	4	As above	NA[b]	NA	NA	NA
Ras Abu Fontas	As above	2	As above	As above	NA	NA	NA
United Arab Emirates							
Abu Dhabi							
Umm Al Nar East	290,900	10	NA	NA	NA	NA	NA
Unit No. UAN—E II	950	1	90	NA	90	Havegap LP (3.5–4)	NA
Unit No. UAN—W IV	750	1	90	NA	90	Belgrad EV 2000	NA
Unit No. UAN—E I	950	1	90	NA	90/95	As above	NA
Unit No. UAN—W III	750	1	90	NA	90/95	As above	NA
Sultanate Oman							
Ghubrah	18,000/27,250	91/113	Polyphsphate/ acid	90/100	Belgrad EV	Belgrad EV (2.5–3)	NA

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[a] TBT: top brine temperature.

[b] NA: not available.

[c] HTA: high temperature additive.

Table 2
Comparison of acid and additive dosing

Acid	Additives
1. Plants smaller, lower plant cost	Plants larger, higher plant cost
2. Longer operating time between cleaning	Requires frequent cleaning, especially if onload system is not employed
3. Lower quantity of noncondensable gases released in the shell	Greater amount of noncondensable gases released in the shell. Higher corrosion of vapor space
4. External decarbonator is required to remove carbon dioxide	Decarbonator not necessary. However, decomposition of bicarbonate ions makes it imperative that the venting system be properly designed
5. Top temperature 121°C	Top temperature 121°C for high-temperature additives, 90°C for polyphosphate treatment
6. Higher heat transfer coefficients. Lower fouling allowance	Lower heat transfer coefficients. Higher fouling allowance
7. Higher thermal efficiency	Lower heat transfer coefficient
8. Smaller pumps	Larger pumps
9. More sophisticated feed treatment	Simple feed treatment
10. Severe corrosion if pH and oxygen level not maintained. Circulating brine pH is 7.5–8. Proper dosing and control is extremely important	Corrosion is less since pH of treated brine is 8.9–9. Overdosing not as harmful as with acid overdosing
11. Corrosion products can accumulate in the tubes with reduction of heat transfer coefficient	Soft deposition occurs, which requires removal by onload cleaning or by acid cleaning
12. Cost varies from $80–250/t	Cost varies up to $3,400/t for HTA. Polyphosphate $600–1,200/t
13. Feed rate: HCl 228–274 ppm of the feed for 32% HCl. 100–120 ppm for H_2SO_4. Equivalent to 1.5 t per million gallons of product	Feed rate varies from 3 to 10 ppm, equivalent to 90–3,000 lb/million gallons of product. HTA dosing rate Almost doubles if top temperature is increased from 100 to 118°C (4–8 ppm)
14. Safety requires careful handling	Relatively safe
15. Shorter service life	Longer life
16. Maintenance intensive	Potential for savings through reduced maintenance cost and shutdowns
17. Large storage capacity required	Smaller storage facilities required

The percentage precipitation for a specific precipitated ion was calculated using Eq. (1).

$$\text{Scale precipitation } \% = (\text{C ion}_{\text{intial}} - \text{C ion}_{\text{final}})/\text{C ion}_{\text{intial}} * 100 \qquad (1)$$

where C $\text{ion}_{\text{intial}}$ is the initial concentration of the precipitated ion as calcium, magnesium, sulfate and bicarbonate ion and C $\text{ion}_{\text{final}}$ is the final concentration of the precipitated ion after 15 min of operation.

The test procedure mainly depends on evaluating the inhibitor at fixed dosing rates under a set of conditions (brine water temperature and concentration of brine water).

The experiments were conducted on normal seawater and two brine solution with CF of 1.5 and 2.0 times normal Gulf seawater. The chemical composition of normal seawater used in the experiments is shown in Table 3. The electrical conductivity of the normal seawater at Doha was 65,000 μs/cm, while the 1.5 and 2.0 brine solutions have electrical conductivity rates of 91,000 and 110,000 μs/cm, respectively. The two brine water solutions were prepared at DRP laboratory using rotavapor system (R-153). The rotavapor system is essentially a distillation unit, which consists of electrical heating bath, rotating evaporation flask, condenser, and vacuum system (Fig. 2).

Four types of antiscalants chemicals (A, B, C, and D) were used to determine the scaling tendency using different types of solutions (seawater, brine water, and concentrated brine). Chemical A is a thermal desalination dispersant and antiscalant with a high-temperature operation and a high specific gravity of 1.3 mg/l. The manufacture of Chemical A claimed that

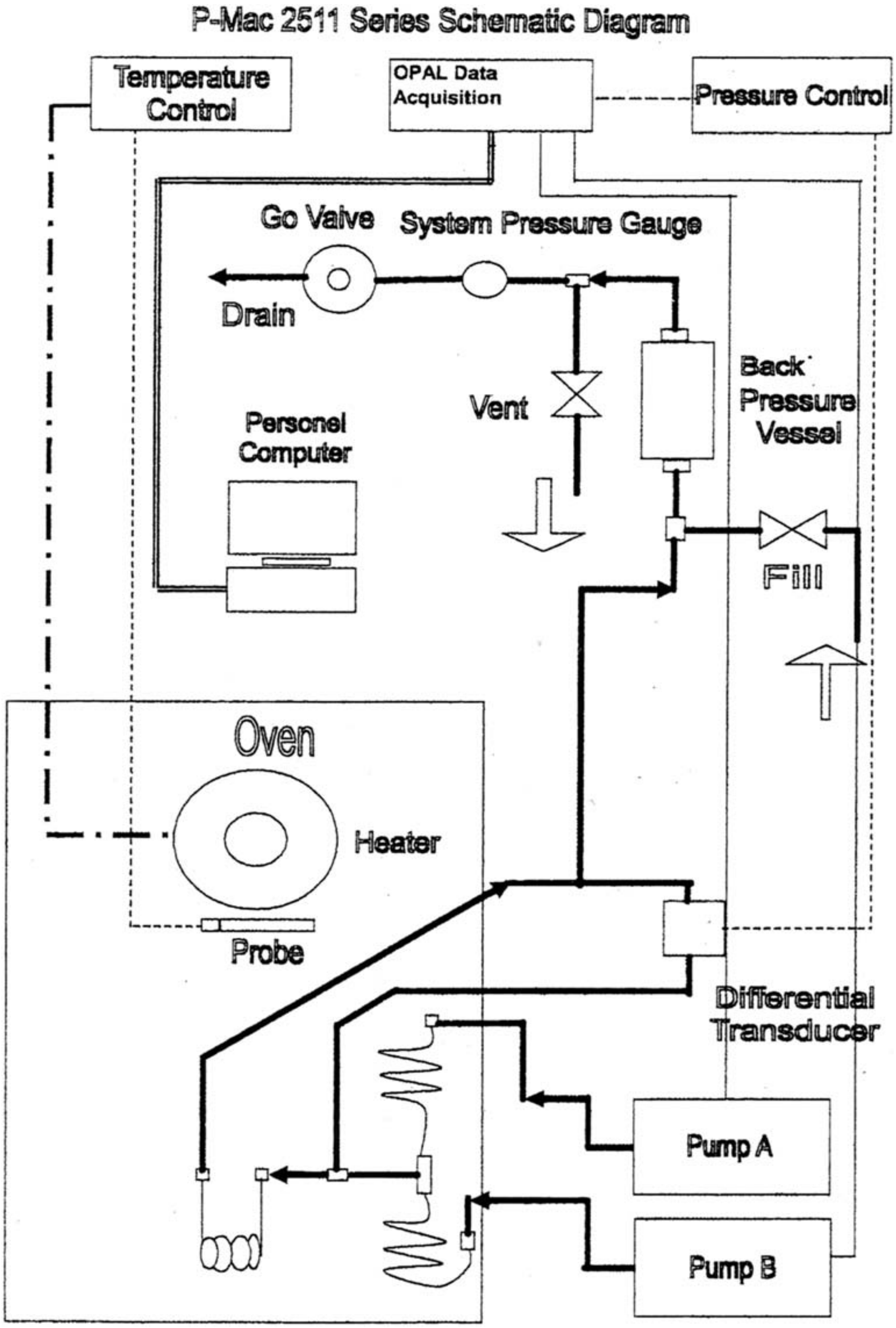

Fig. 1. Schematic diagram of OP-Mack 2500 device.

the chemical are stable up to 160°C. Chemical B is an antiscalant formulated for feedwaters with the highest level of meta oxides, silica, and scale-formatting minerals. The manufacturer of this antiscalant promised that it can effectively control inorganic scales over a large concentration range, and can control $CaCO_3$ and calcium sulfate scales. The manufacturer stated that this chemical is stable up to 260°C. Chemical C is a

Table 3
The chemical composition of Beachwell seawater at Doha site

Parameter	Beachwell Seawater		Standard deviation	Maximum	Minimum
pH	7.43	±	0.15	7.67	7.06
Temp (°C)	27.38	±	0.89	30.00	25.80
Conductivity (ms/cm)	65.14	±	1.05	67.30	61.60
TDS (mg/l)	47952.00	±	3298.00	55166.00	40649.00
Turbidity	0.54	±	0.50	1.00	0.00
Ca^{2+} (mg/l)	1021.48	±	80.00	1280.00	800.00
HCO_3^- as $CaCO_3$	129.47	±	6.3	146.00	113.00
Cl^- (mg/l)	25031.0	±	1513.00	30400.00	22400.00
Total Hardness	8728.88	±	324.00	9320.00	8040.00
Mg^{2+} (mg/l)	1527.25	±	112.00	1965.00	1351.00
SO_4^{2-} (mg/l)	3680.00	±	123.00	4200.00	3500.00
PO_4^{3-} (mg/l)	0.23	±		0.59	0.05
NH_4 (mg/l)	0.00	±		0.00	0.00
NO_3 (mg/l)	2.06	±		3.00	0.80
SiO_2 (mg/l)	6.15	±	2.00	12.60	3.30
F^- (mg/l)	4.23	±	1.50	7.00	1.94
Na^+ (mg/l)	16239.00	±	817.00	19722.00	14532.00

liquid product to control a scaling of seawater in MSF distillation plants. It is a bend of organophosphonate, polymaleic, and polyacrylate copolymers. C has been especially designed to enhance scale control, and is also considered as a dispersing agent to reduce cleaning frequencies and the associated costs. Chemical D is a dispersing agent; its chemical name is maleic acid copolymer sodium salt. It is used as a scale inhibitor with a specific gravity of 1.27. All these chemicals were tested in OP-Mack instruments at different operating temperatures of 120, 140, and 160°C respectively and different concentration of seawater with antiscalant or without using any type of chemicals. The four additives were tested using seawater, brine water with CF of 1.5 times seawater, and the concentrated brine with CF of 2.0 times seawater.

4. Results

Figs. 3–5 shows the percentage precipitation of main ions for seawater, without using any antiscalant, and also represents the percentage precipitation of precipitated ions and at a dosing rate of 5 ppm of the four tested antiscalant chemicals (A, B, C, and D) using seawater solution at 120, 140, and 160°C, respectively. While Figs. 6–8 represents the percentage precipitation of precipitated ions and at different dosing rate of different antiscalant chemicals using brine solution (CF of 1.5) at 120, 140, and 160°C, respectively. Furthermore, Fig. 9 represents the percentage precipitation of ions using concentrated brine solution (CF of 2) at different temperatures and different concentration of chemicals.

5. Discussion of results

5.1. Concentration factor and scaling without antiscalant

As can be seen from the general trend in figures reveals that as the concentration of the tested solution increases the percentage precipitation of the precipitated ions increases. The percentage precipitation of the Ca^{2+} ion increased from about 8.91% at 120°C for seawater to 13.64% at the same temperature, but with higher salinity tested brine solution (CF 1.5 times seawater), and finally reached 18.55% precipitation with concentrated brine (CF 2.0 times seawater). Even though the percentage precipitation of bicarbonate ion decreased with increasing temperature, its percentage precipitation increased with increasing the salinity of the tested solution. The percentage precipitation of bicarbonate ion for seawater at 120°C was 18.72% and increased to 23.89% for brine solution, until it reached a 26.35% with concentrated brine solution.

This result agrees with the result obtained by Dooly and Glater [11] who studied the effect of increasing solution salinity with the weight of the alkaline scale precipitated, and reported an increment in the weight scale of both $Mg(OH)_2$ and $CaCO_3$ as the solution CF increased. Similar result was observed for the precipitation of sulfate and magnesium ions, where the

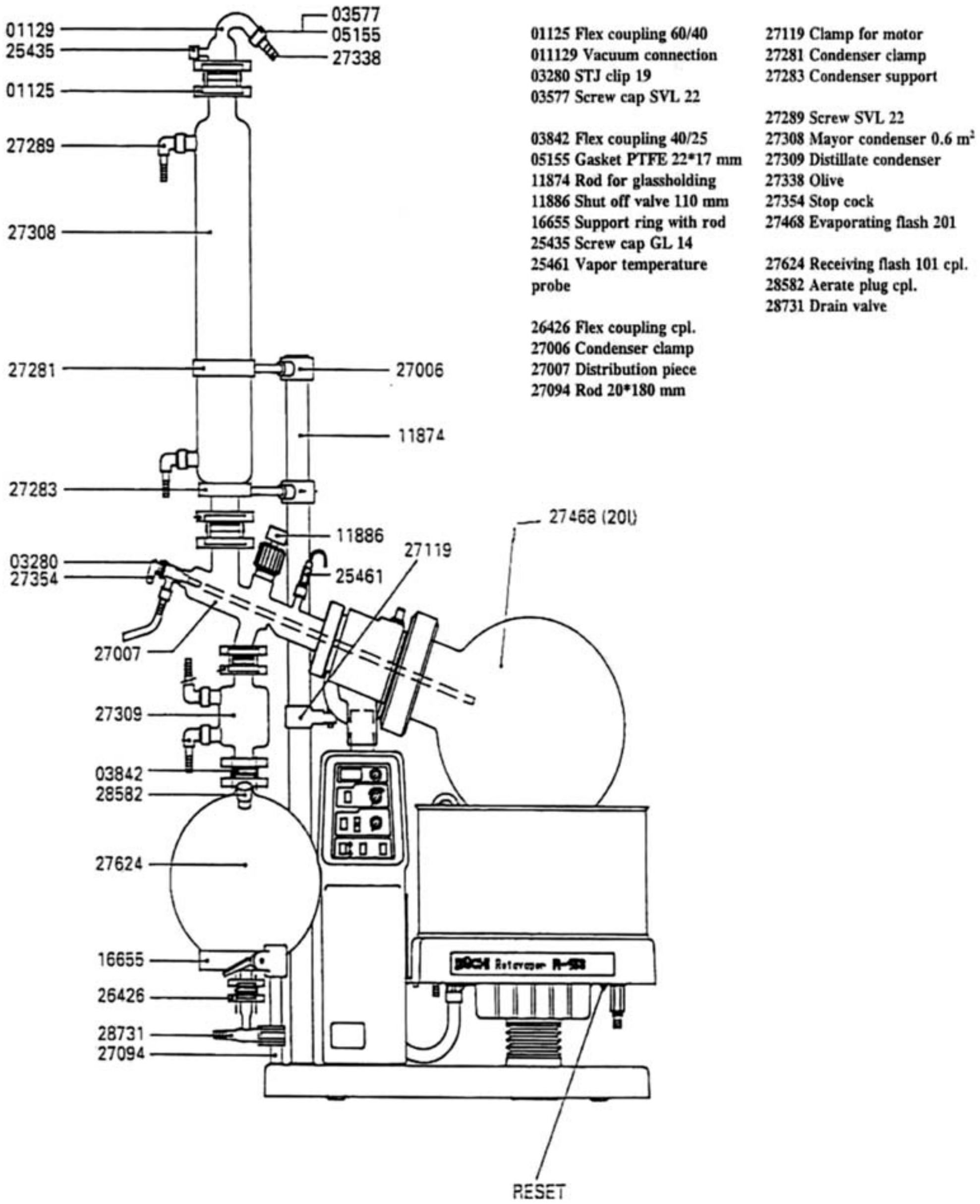

Fig. 2. Schematic diagram of Rotavapor (R-153) device.

percentage precipitation of the magnesium and sulfate has increased with the increasing salinity of the tested solution (Figs. 3, 6, and 9). The percentage precipitation of sulfate was found to be slightly increased from 20.28% for seawater to 22.98% for brine water (CF 1.5 seawater), and finally increased to 25.5% with concentrated brine at the same temperature.

It is worth mentioning that calcium sulfate precipitation is not a function of pH. Calcium sulfate scaling is a result of a fundamental chemical process occurring only when the solubility limits of this compound are exceeded. The solubility limit can be reached only when concentrating the brine (increasing the saturation level to reach the solubility limit), or raising its temperature [12]. Increasing the scaling as the salinity increased may refer to the solubility product (Ksp) and its complications when the precipitated salt is present in a mixed system. It well known that the different salinity levels have no effect on the thermodynamic solubility constant (Ksp) of pure salts. On the other hand, for mixed systems in which more than one salts existed, the Ksp of the mixed system is influenced by the salinity levels. This is believed to be due to the effect of salinity on the polymorphism and

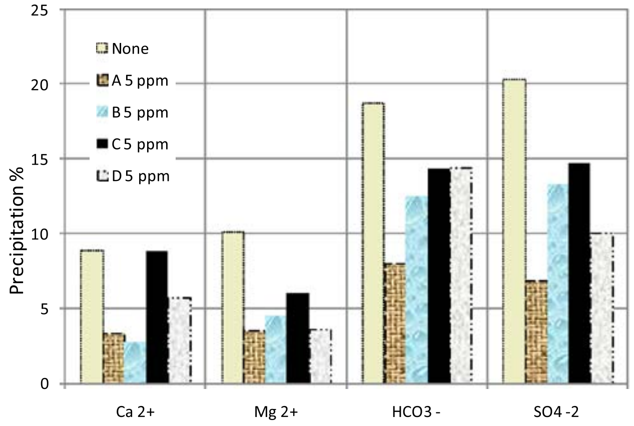

Fig. 3. The percentage precipitation of precipitated ions at 120°C and at a dosing rate of 5 ppm of different antiscalant chemicals using seawater solution.

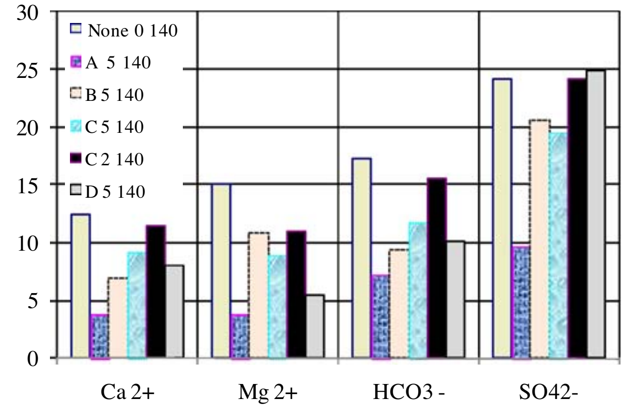

Fig. 4. The percentage precipitation of ions at 140°C and at a dosing rate of 5 ppm of different antiscalant chemicals using seawater solution.

crystal habit [13–15]. Shams El-Din and Rizk [16] also reported that the analysis of the samples of the mud collected from brine heater section on a real MSF plant revealed that the deposit is not a single compound, but it is formed from a number of scale forming substance. Where 20.8% of the scale deposit is calcium and 45% was bicarbonate, only 8.7–9.2% was magnesium ion at operating temperature of 90°C.

5.2. Temperature and scaling without additives

Similar trend was also noticed as the operating temperature was increased from 120 to 160°C. As shown in Figs. 6–8 the percentage precipitation of calcium for brine water has increased from 13.64% at 120°C (Fig. 6) to 18.58% at 140°C (Fig. 7), and finally reached 26.25% at 160°C (Fig. 8). The scaling tendency of the precipitated ions was found to increase with increasing temperature. This result was reported by Dyer and Graham [17]. Jasbir [10] also reported that high operating temperature in MSF evaporators causes formation of hard tenacious scale from calcium sulfate anhydrite, mineral scale such as $CaCO_3$, Mg $(OH)_2$, and barium sulfate. Furthermore, high operating temperature increases the homogenous precipitation instead of the heterogeneous precipitation at low temperature [15].

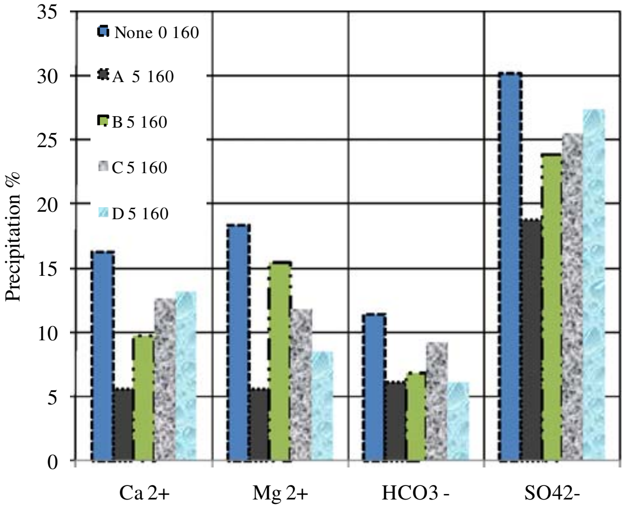

Fig. 5. The percentage precipitation at 160°C and at a dosing rate of 5 ppm of different antiscalant chemicals using seawater solution.

The precipitation trend for the precipitated ion was proven to increase with increasing temperature. However, there were some ions found to precipitate more than the others, especially as the temperatures increased. Overall, the highest percentage of precipitation (43.09%) at 160°C was reported for sulfate ion with concentrated brine solution (Fig. 9), followed by the percentage precipitation of magnesium ions (29.82%) then the percentage precipitation of calcium ions (29.74%), and the bicarbonate ions (17.96%), the lowest ions in precipitation. This implies that the main scaling at high temperature is calcium sulfate followed by $Mg(OH)_2$. The lowest percentage of scaling was found to be the $CaCO_3$. The only percentage precipitation that decreases with increasing temperature was the bicarbonate ion. This is because the conversion of HCO_3^- to carbonate ions (CO_3^{2-}) as shown (Reaction 1) occurs mainly at low operating temperature, and the result of $CaCO_3$ scaling ($CaCO_{3(s)}$) as presented in Reaction 2, while the conversion of CO_3^{2-} to OH^- (Reaction 3) is expected to occur more at a temperature greater than 80°C [18] and the result of $Mg(OH)_2$ scaling formation as shown in Reaction 3.

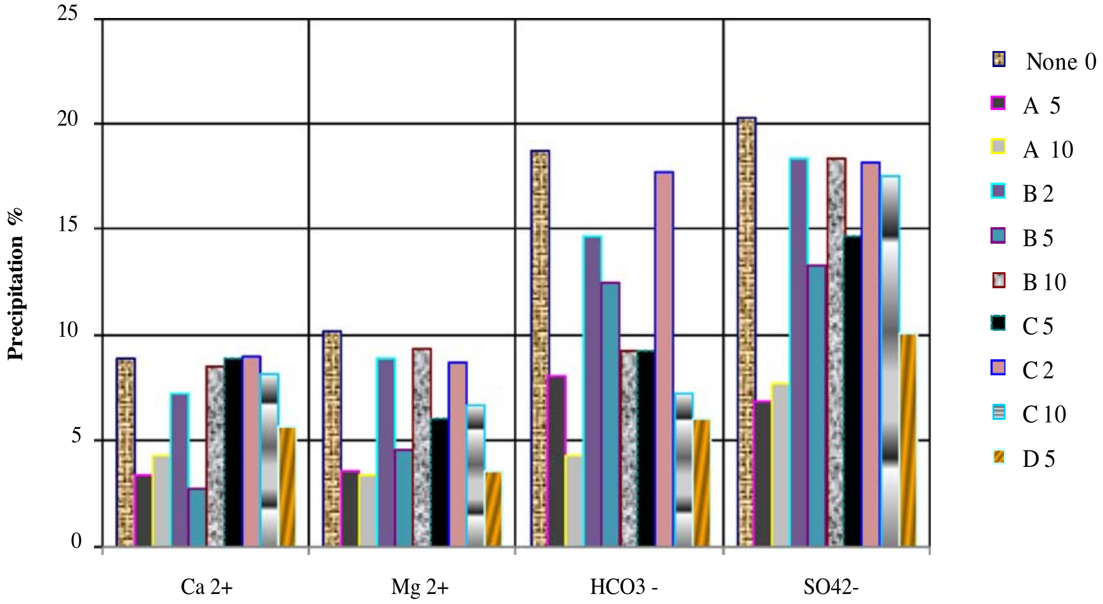

Fig. 6. The percentage precipitation of ions using brine solution at 120˚C at different concentration of chemicals.

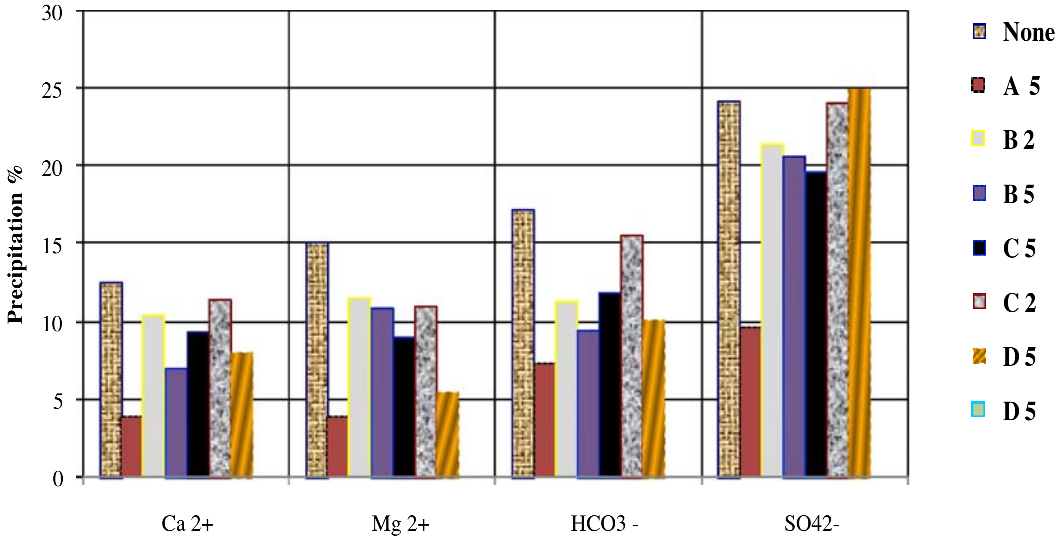

Fig. 7. The percentage precipitation of ions using brine solution at 140˚C at different concentration of chemicals.

$$2HCO_3^- \rightarrow CO_3^{2-} + H_2O + CO_2 \quad \text{(Reaction 1)}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)} \quad \text{(Reaction 2)}$$

$$CO_3^{2-} + H_2O \rightarrow CO_2 + 2\ OH^- \quad \text{(Reaction 3)}$$

Amor et al. [15] and Hiller [19] investigated the precipitation kinetics of $CaCO_3$ at different temperature, and they reported the precipitation of $CaCO_3$ at high and low temperature. The $CaCO_3$ and $Mg(OH)_2$ have inverse solubility, i.e. as the operating temperature increased, their solubility decreased, and as the temperature increased the nucleation rate was also increased. Dooly and Glater [11] reported the percentage composition of alkaline scale formed at different high operating temperatures, where the percentage precipitation of $CaCO_3$ scaling was found to decrease with increasing temperature, while the percentage precipitation of $Mg(OH)_2$ increased with

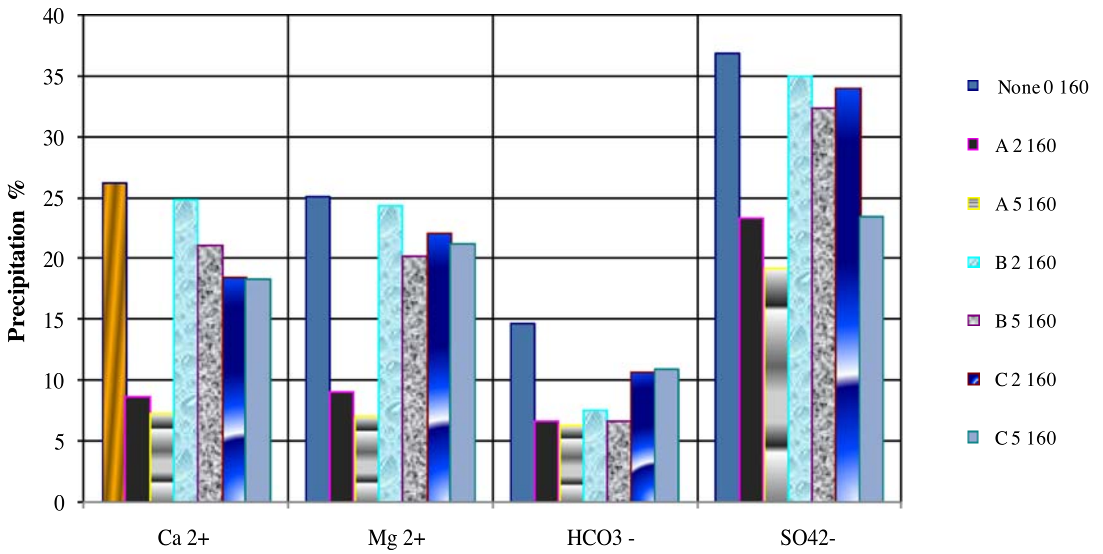

Fig. 8. The percentage precipitation of ions using brine solution at 160°C at different concentration rates of chemicals.

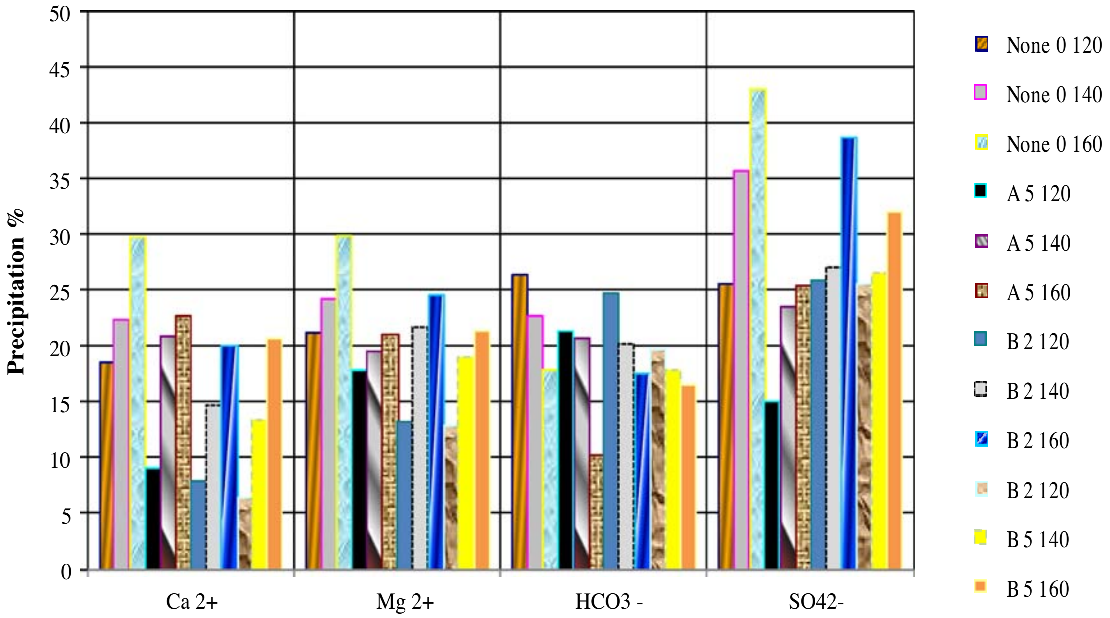

Fig. 9. The percentage precipitation of ions using concentrated brine solution at different temperature and different concentration of chemicals.

increasing operating temperature. Dooly and Glater [11] are in agreement with result obtained in this project. The formation of $CaCO_3$ and $Mg(OH)_2$ in seawater also depends on many factors, namely temperature, pH, concentration of bicarbonate ions, rate of CO_2 release, concentration of calcium to magnesium ions ratio (Ca^{2+}/Mg^{2+}), the concentration of carbonate to hydroxyl (CO_3^{2-}/OH^-) ratio, and TDS [9,20]. The (CO_3^{2-}/OH^-) ratio is very sensitive to temperature change, which explains the normal gradual reduction in $CaCO_3$ precipitation with increasing temperature and the gradual rise in the precipitation of $Mg(OH)_2$ above 80°C [21].

The sulfate scaling was increased with increasing temperature. The percentage precipitation of sulfate scaling for seawater at 120°C was found to be 20.28% and then increased to 24.16% at 140°C (Fig. 3), until it reached 30.18% at 160°C (Fig. 5).

Marshall et al. [12] reported similar result, and explained the inverse solubility of the three different forms of calcium sulfate. As the temperature increased the Ksp was found to decrease, and result of increasing the scaling tendencies of calcium sulfate increased.

5.3. Additives and temperatures

As shown in Fig. 3, antiscalant A at 120°C was the most effective in reducing scale tendency among other used chemicals. Chemical A succeeded in reducing the percentage precipitation of sulfate ions from 20.28% without antiscalant to about 6.86%, followed by chemical D which also succeeded in reducing the percentage precipitation of sulfate ions to about 10.09%. Chemicals C and B can also be considered effective in reducing sulfate scaling where they reduce the scaling tendency to 14.65 and 13.27%, respectively, with a 5 ppm dosing. It is obvious that chemical A has reduced the scaling potential for all other scaling species; it reduced the percentage precipitation of calcium ions from 8.91 to 3.33%. The percentage precipitation of magnesium was also decreased from 10.16 to 3.55%, and finally, the bicarbonate percentage precipitation from 18.72 to 8.01%.

Chemical D followed chemical A in its performance, while chemicals B and C seemed to be very close in their performance at 120°C.

Fig. 4 shows the performance of the four chemicals at 140°C at a dosing rate of 5 ppm. Again, chemical A showed good performance compared to the other chemicals, followed by chemical D for the calcium and magnesium ions, but chemical D failed in preventing sulfate scaling at 140°C. Chemical D showed the same percentage precipitation without using any scaling inhibitor (24%) (Fig. 4). This implies that chemical D loses its effectiveness as the temperature increases above 120°C. Chemical B reduced the percentage precipitation of calcium ions from 12.5 to 10.37%, where chemical C reduced it to 9.22%, and chemical D reduced it to 8.02%. The best reduction was obtained when using a 5 ppm of chemical A, where the percentage precipitation was reduced to 3.84%.

For the bicarbonate ion, chemical A reduced the percentage precipitation potential of this precipitated ions from 17.23% at 140°C to 7.25%, whereas chemical B reduced it to 9.43%, followed by chemical D with a percentage precipitation reduced to 10.15%, and finally chemical C with reduction to 11.83%.

Similar trend was noticed for the magnesium ion precipitation, where chemical A reduced the percentage precipitation of magnesium from 15.1% without antiscalant to 3.87%, followed by chemical D to 5.5%, then chemical C to 8.96%, and finally to 11.5% for chemical B.

Fig. 5 shows the performance of the tested chemicals using seawater at 160°C. Chemical A also proved its reliability in preventing the scaling of seawater solution where it reduced the percentage precipitation of sulfate ion from 30.18 to 18.74%. This was followed by chemical B which reduced the percentage precipitation of sulfate scaling to 23.86%, then chemical C which reduced the percentage precipitation to 25.5%, and finally chemical D reducing the scaling potential to about 27.29%.

Results imply that chemical D is not effective in controlling sulfate scaling as the temperatures increased to greater than 120°C (Fig. 5), thus, losing its effectiveness.

Chemical A also succeeded in reducing the percentage precipitation of calcium ion from 16.29 to 5.62%, and chemical B reduced the percentage precipitation of calcium to 9.70%. Furthermore, chemicals C and D reduced the percentage precipitation of calcium ion from 16.26% without chemical to 12.68 and 13.15%, respectively. The percentage precipitation of magnesium ions has been reduced from 18.29% to about 5.57% using chemical A, to 8.50% using chemical D, to 11.84% using chemical C, and finally to 15.44% using chemical B.

This implies that chemical D is still effective even though at high operating temperature at 160°C to prevent alkaline scaling (bicarbonate and magnesium ions) with seawater solution, but it lost its effectiveness in preventing sulfate scaling as the temperature increased to above 120°C.

5.4. Additives and salinity

An additive in brine solution at 120°C is shown in Fig. 6. The minimum calcium precipitation was obtained when using chemical B at a dosing rate of 5 ppm, followed by chemical A at the same dosing rate. The maximum precipitation was obtained when using chemical C at a dosing rate of 2 ppm and with a percentage precipitation of 12.81% (Fig. 6). Chemical A was found to be the best antiscalant in preventing magnesium precipitation in brine solution. The optimum dosing rate of chemical A was 10 ppm. Magnesium precipitation was reduced to 3.51% with 10 ppm of chemical A. The highest precipitation (10.65%) was obtained when using chemical C with a dosing rate of 2 ppm (Fig. 6). Again, chemical A was the best antiscalant and showed the highest performance among other chemicals in preventing bicarbonate scaling even at high temperature as 120°C, while the performance of chemicals B and C were close to none scaling performance (Fig. 7). Chemical B showed different behaviors, as it prevented calcium precipitation in a high percentage at 120°C, and failed in preventing the other ions in the same manner and especially at a low dosing rate of 2 ppm. However, chemical B represented a better performance considering an increase in the concentration of the dosing rate to 5 ppm. Finally, the performance of chemical C in preventing or reducing scale formation was much lower than chemicals A and B.

5.4.1. Additives in brine solution at 140°C

For brine solution at 140°C, it is clearly seen in Fig. 7 that the minimum calcium, sulfate, and magnesium ions precipitation were obtained using chemical A at a dosing rate of 5 ppm. The percentage precipitation of those ions (calcium, sulfate, and magnesium) showed 4.4, 9.29, and 3.96%, respectively. The highest percentage precipitation achieved for these ions was by utilizing chemical B with a dosing rate of 2 ppm.

5.4.2. Additives in brine solution at 160°C

The brine solution was also tested at a high temperature of 160°C. The percentage precipitation of precipitated ions—calcium, magnesium, bicarbonate, and sulfate—were increased even with using chemicals.

But, the minimum percentage precipitation was achieved by chemical A at a dosing rate of 5 ppm, whereas the percentage precipitation levels of calcium, magnesium, bicarbonate, and sulfate were 7.29, 7.04, 6.37, and 19.29%, respectively (Fig. 8). Chemical A reduced the percentage precipitation of sulfate from 36.8 to 19.29%, while chemical B achieved almost the same level of precipitation when no chemical was used, i.e. chemical B failed in preventing sulfate scaling in brine solution. Chemical C reduced the percentage precipitation of sulfate scaling from 36.8 to 34.06% at 2 ppm and to 23.41% at 5 ppm. Although chemical C performed well in preventing sulfate scaling, its effect on reducing the bicarbonate and magnesium precipitation was very low, reducing the magnesium precipitation from 25.05% to only 21.24% and the bicarbonate precipitation from 14.61% to only 10.84%.

Result implies that some chemicals can be effective in preventing sulfate scaling, but they may not be effective in preventing all types of scaling.

All chemicals showed similar trend in their behavior with increasing the concentration. Chemicals A, B, and C with concentration of 5 ppm showed better performance than 2 ppm in lowering scale formation for all ions.

5.5. Concentrated solution at different temperatures

When concentrated solution was tested without the chemicals, the percentage precipitation increased, but when chemicals were used, the percentage precipitation decreased.

At 120°C, chemical B achieved the lowest percentage precipitation of calcium, magnesium, and bicarbonate scaling, reducing the percentage precipitation level to 6.4, 13.02, and 19.7%, respectively. Chemical A achieved the lowest percentage precipitation in sulfate scaling at 15.09% (Fig. 9).

The minimum percentage precipitation at 140°C was 13.41% for calcium ion, 19.01% for magnesium ion, and 17.82% for bicarbonate ion when using chemical B. The lowest percentage precipitation of sulfate ions was obtained when using chemical A, showing the effectiveness of chemical A in reducing sulfate scaling even at high salinity and high operating temperatures.

At 160°C, the minimum percentage precipitation of calcium ion was 20.75% achieved when using chemical B, while the minimum percentage precipitation levels of magnesium, bicarbonate, and sulfate were 21.08, 10.29, and 25.34%, respectively, obtained with chemical A. Based on the previous result at 160°C, the effectiveness of chemical B decreases as the temperature increased.

6. Conclusions

Based on the results of this project, the following conclusions were drown:

- The percentage precipitation of sulfate, calcium, and magnesium ions scaling were found to increase with increasing temperature, while the bicarbonate ion was the only ion which decreased when increasing the temperature above 120°C. However, the scaling potential for all scaling species were found to be affected by the concentration of the tested solution, and the level of salinity increased, as the percentage precipitation increased.
- Chemical D was not effective in controlling sulfate scaling as the temperatures increased above 120°C. However, it was effective even at high operating temperature at 160°C to prevent alkaline scaling (bicarbonate and magnesium ions) with seawater solution.
- Chemical B was effective in reducing scaling when using high-salinity water and at low operating

temperature, but it lost its effectiveness as the temperature increased to more than 140℃.

- Chemical A was effective in reducing sulfate scaling even at high-salinity or high-temperature operation up to 160℃. This chemical showed superior effectiveness in reducing different types of scaling when using seawater and brine solution at high operating temperature, but its performance was slightly decreased when the concentration of the solution was increased. Although chemical A was the most expensive chemical, it is recommended, since it can increase the production of MSF plants, reduces the energy cost, and reduces the maintenance cost.
- None of the tested antiscalant can eliminate sulfate scaling totally at high operating temperatures, although chemical A succeeded in reducing sulfate scaling, it cannot eliminate it totally.
- Chemical C was found to be effective in preventing alkaline scaling, but it was failed completely in preventing sulfate scaling even at l20℃. In general, the performance of chemical C in preventing or reducing scale formation was much lower than the other chemicals tested in this project.
- A comparison of the inhibitors and scales showed that a universal inhibitor for all kinds of scale does not exist. One inhibitor maybe better for prevention of $CaCO_3$ scale than for calcium sulfate; different inhibitors have different degrees of effectiveness even for various hydration form of the same scale.

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