



A comparative study of novel scale inhibitors with commercial scale inhibitors used in seawater desalination



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HIGHLIGHTS

- Loss of Ca^{2+} from seawater was followed in the presence of inhibitors.
- Novel poly(acrylic acid) scale inhibitor performance depended on end-group.
- Mid-length end-group at low molar mass outperformed commercial inhibitors.

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ABSTRACT

Seawater from the Arabian Gulf was heated under conditions simulating those of thermal desalination processes and the change in the amount of aquated Ca^{2+} followed over time using Inductively Coupled Plasma/Optical Emission Spectroscopy. This was done in the absence of any scale inhibitor, and in the presence of scale inhibitors: three commercial polycarboxylate products commonly employed in thermal desalination plants and four novel poly(acrylic acid) inhibitors of differing molar masses and end-group functionality. At times >2 min, the novel poly(acrylic acid) scale inhibitors of low (~2000) molar mass and moderate (hexyl isobutyrate or cyclohexyl isobutyrate) end-group hydrophobicity were more effective in maintaining the aquated Ca^{2+} level than any commercial product.

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1. Introduction

The production of fresh water from seawater in thermal desalination plants using processes such as multi-stage flash (MSF) and multiple-effect desalination (MED) is normally accompanied by deposition of scale such as calcium carbonate (CaCO_3), magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and calcium sulfate (CaSO_4) on heat transfer surfaces. If not controlled, this can result in serious loss of efficiency and the loss of production makes periodic shut-down of the plant for cleaning essential [1,2].

To control the problem of scaling on heat transfer surfaces in MSF plants, several scale control prevention methods have been adopted. The most popular methods are (a) acid treatment; (b) additive treatment; and (c) mechanical cleaning [3,4]. Chemical scale inhibitors have gained importance over recent decades due to their ease of handling, low dose rate, minimal corrosion problems and relatively low cost [5]. The primary method used historically in MSF desalination

plants to control scale formation has been acid treatment. In this seawater treatment, the pH of seawater is maintained around 4.5 using acid, most often H_2SO_4 due to its low cost. At this pH the equilibrium between the scale-forming CO_3^{2-} and OH^- anions and their soluble protonated forms CO_2 and H_2O and lies far toward the uncharged species. Careful control of the pH is essential: falling below pH 4.5 will lead to corrosion, while any increase will give reduced control of scale formation. CaSO_4 , however, is not eliminated by this treatment [3]. Mechanical cleaning by sponge ball cleaning or Tapproge system is usually used in combination with a scale inhibitor to wipe heat transfer tubes in situ and prevent the adherence of scale [4].

1.1. Polymeric scale inhibitors

Scale inhibitors are chemical additives used to control the formation and/or deposition of scale. Unlike acid treatment, they can impact on the formation of CaSO_4 as well as alkaline $\text{CaCO}_3/\text{Mg}(\text{OH})_2$ scale. Clearly, the efficiency of scale inhibitors will depend on parameters of the system to which they are applied (ion concentration, temperature pH, pressure), on their chemical properties (functionality, molecular mass,

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polydispersity, structure) and on how they are used (concentration, method of application). The type of scale inhibitors and dosing rate are very important operating parameters in desalination. Less than optimum dosing rate of scale inhibitors leads to scale formation, while overdosing can enhance sludge formation [6]. The level of addition has been progressively reduced over the past few years, sometimes to below 1 ppm [5].

Most scale inhibitors are polymeric and there are three common groups of polymeric scale inhibitors.

1. Polymers containing phosphate groups, such as polyphosphate esters, polyphosphonates and polyphosphates.
2. Polymers containing sulfonate groups, such as poly(sulfonic acid) and poly(ethylene sulfonic acid)
3. Polymers containing carboxylic acids such as poly(acrylic acid) and poly(maleic acid).

Many types of polymeric inorganic phosphorus (polyphosphate), organic phosphorus compounds (e.g., 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP)), and polyphosphonate additives effectively inhibit scale formation [7]. In general, linear polyphosphates hydrolyze readily between 70 and 90 °C and so are less effective in thermal desalination [8]. Phosphonate compounds contain phosphonic groups bound directly to a carbon atom on an organic compound. Polyphosphonates are more resistant to the hydrolysis than polyphosphate due to the very strong bond between carbon and phosphorus [9].

Polysulfonate scale inhibitors are not employed commercially to a great extent in thermal desalination but show promise for controlling scale formation at elevated temperatures, as the carbon–sulfur bond is resistant to hydrolysis [10].

Poly(carboxylic acid)s such as poly(acrylic acid) (PAA) poly(methacrylic acid) and polymaleic acid with molar masses in the region of 2000–4000 are effective species in preventing scale deposition in desalination [11]. Over this range of molar masses, PAA is the most common scale inhibitor used for water treatment in desalination [12].

An important property of these polymers is that they have good thermal stability in the normal operation conditions for thermal desalination plants (90–110 °C). As well as being effective in preventing the deposition of the scale formed by hard water salts, they are extremely effective dispersing agents for suspended solids [13].

1.2. Objectives of this research

The aim of this work was to determine the efficiency of novel end-group-modified poly(acrylic acid) (PAA) scale inhibitors, which we have previously found to be of promising effectiveness in laboratory studies of salt solutions [14,15], in preventing calcium carbonate deposition in treated concentrated seawater (Table 1) at 104 °C. The efficiency of these novel scale inhibitors under these conditions was compared with commercial scale inhibitors that have been shown to

have a good efficiency in controlling scale formation used in thermal desalination plants of the Saline Water Conversion Corporation (SWCC), Saudi Arabia.

1.3. Selection of scale inhibitors

Four scale inhibitors investigated in our previous studies were selected for application in this study [15]. The two scale inhibitors found to be best in preventing CaCO₃ scale formation in bulk solution in our previous studies are low molar mass PAA with mid-length hydrophobic end groups (hexyl isobutyrate-PAA, $M_n = 1400$, HIB-PAA; and cyclohexyl isobutyrate-PAA, $M_n = 1700$, CIB-PAA). Low molar mass PAA with a long end group (hexadecyl isobutyrate-PAA $M_n = 1700$, HDIB-PAA) which did not inhibit crystallization in the bulk, but was excellent in preventing deposition of CaCO₃ on surfaces, was also chosen for investigation, as was a higher molar mass PAA with mid-length hydrophobic end groups (hexyl isobutyrate-PAA, $M_n = 3600$), chosen to study the impact of molar mass on inhibition performance.

Three commercial polymeric scale inhibitors commonly used in MSF plants in Saudi Arabia were selected for comparison. Albrivap DSB(M), a phosphonate-based scale inhibitor; Belgard EV2030, a polycarboxylate scale based on poly(maleic acid) copolymer; and Sokalan EP10i, another polycarboxylate based on a poly(maleic acid) copolymer.

Trials of these commercial scale inhibitors in MSF had been previously carried out at Doha West and at the Al-Zour power generation and water production station [13]. The results showed that Albrivap DSB(M) is quite effective and successful in controlling scale formation at top brine temperature (TBT) of 103 °C and dose rate of 3.0 ppm, Belgard EV2030 at TBT of 105 °C and dose rate of 1.5 ppm and Sokalan PM10i at a TBT of 105 °C and dose rate of 1.5 ppm during the 3 month test period [13].

Tests of these three commercial scale inhibitors were also performed in SWCC's Saline Water Desalination Research Institute (SWDRI) MSF pilot plant for one month at TBT of 112 °C and dose rate of 2 ppm and at the Jeddah IV commercial plant for six months at TBT of 110 °C at the same dose rate [16]. The results of these tests showed that Belgard EV 2030 was found to be effective in controlling scale in brine heater tubes but no outstanding improvement was shown in reducing demister pads fouling. Based on this evaluation Belgard EV 2030 was approved for using as scale inhibitor in MSF plants [16].

2. Materials and methods

The PAA scale inhibitors used were prepared by Atom Transfer Radical Polymerization of poly(*t*-butyl acrylate) and characterized as previously reported [17]. Albrivap DSB(M) (Solvay), Belgard EV 2030 (BioLab) and Sokalan PM10i (BASF) were purchased from the manufacturers and used as supplied. Sodium carbonate (AnalaR), hydrochloric acid (BDH) and sodium hydroxide (AnalaR) were used as supplied. Raw seawater was obtained from Al-Jubail Desalination Plant (Arabian Gulf) in Saudi Arabia.

3. Experimental

A solution of 0.167 M (10,000 ppm) of CO₃²⁻ as Na₂CO₃ (Analar) was prepared by adding 17.702 g of Na₂CO₃ to 1 L volumetric flask. PAA solutions were prepared by dissolving 0.010 g of PAA in 20 mL water (500 ppm) and were used within three days of preparation. Commercial scale inhibitor solutions were prepared by dissolving 1 g of the commercial solution in 1 L distilled water (500 ppm, the concentration of commercial solution of scale inhibitor is usually between 40 and 50% w/w). These solutions and the R/O water used were filtered and degassed using a 0.45 μm Millipore solvent filter.

Table 1

Treated seawater composition (as part per million, ppm). TDS: Total dissolved solids. ICP/OES: Inductively Coupled Plasma/Optical Emission Spectroscopy.

Ions	Concentration (ppm)	Method of analysis
TDS	45,325	Evaporation Method-AWWA STD Method #2540C
pH	8.2	AWWA STD Method #2540C
Na ⁺	13,200	ICP/OES AWWA STD Method ^a #3125 B
Ca ²⁺	546	ICP/OES AWWA STD Method ^a #3111 BC&D
Mg ²⁺	1635	ICP/OES AWWA STD Method ^a #3111 BC&D
K ⁺	521	ICP/OES AWWA STD Method ^a #3111 BC&D
HCO ₃ ⁻	39	Titration AWWA STD Method ^a #2320
SO ₄ ²⁻	3321	HACH Spectrophotometer #8051

^a American Water Works Association, Standard Methods for water and waste water treatment, 20th edition.

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