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Characterization of the inhibitory effectiveness of environmentally friendly anti-scalants

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ABSTRACT

A widely used technique for controlling scale deposition is by dosage of an anti-scalant. Large quantities of polymeric scale inhibitors are used for scale control. Scale inhibition additives are built for long existence and persist for many years after their disposal. Many conventional additives are thought to be environmentally unfriendly. Increasing environmental concerns and discharge limitations have caused scale inhibitor chemistry to move toward "green" anti-scalants endowed with biodegradable propensity. One of the factors hindering the practical application of green biodegradable anti-scalants is the lack of adequate performance data and, in particular, results originating from objective sources. The present study discloses results of a study aiming to advance the awareness of green anti-scalants by publication of reliable objective data. The inhibitory effectiveness of three commercially available green anti-scalants was compared with that of conventional phosphonate-based anti-scalants in two experimental systems operated under scaling conditions: a reverse osmosis (RO) system, equipped with a spiral wound membrane; and a thermal system, equipped with a stainless steel electric heater. The RO tests were conducted using a solution simulating desalination of brackish water prone to $CaCO_3$ scaling and the electric heater system tests were performed using a solution prone to $CaSO_4$ scaling. The RO scaling tests revealed that the inhibitory effectiveness of all tested green anti-scalants approached closely the effectiveness of conventional phosphonate-based anti-scalants. In the thermal $CaSO_4$ scaling tests, only one of the three tested green anti-scalants closely approached the inhibitory effectiveness of a conventional phosphonate based anti-scalant. Overall, the data from both experimental systems indicate a promising potential for the already commercially available green anti-scalants and stress the need for further studies characterizing the inhibitory capabilities of green anti-scalants.

Keywords: Calcium carbonate; Calcium sulfate; Green chemistry; Reverse osmosis

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1. Introduction

Scale deposition is a difficulty encountered with water containing ions of sparingly soluble salts. A scaling potential is encountered when a solution is concentrated beyond the solubility limits of one or more of its constituents by water evaporation (as in water cooling towers) or by separation of pure water at ambient temperature (as in membrane processes). Scale deposition cannot be tolerated because of its highly deleterious effects on production capacity and specific energy consumption. It is, therefore, essential to incorporate in every desalination process a cost-effective scale control technique.

Techniques for preventing scaling rely on elimination or reduction of the scale forming ions and modification of the process conditions such as temperature, flow velocity, and pH. A widely used technique for controlling scale deposition is by dosage of an anti-scalant (AS). The conspicuous advantage of this scale control technique is that, when properly applied, an anti-scalant can suppress scale formation at sub-stoichiometric amounts (typically 0.5–10 mg/L).

Anti-scalants act by affecting mechanisms and rates of processes involved in scale deposition, notably nucleation, crystal growth, aggregation, and phase transformation. The consequence of such effects may be one or more of the following: change in the crystal number and size distribution, habit modification, intercalation of the polymer within the crystal, and change in the type of the precipitating polymorph [1,2]. The AS interaction with a scaling entity is based on adsorption of negatively charged AS molecules on the surface of developing nuclei and on positively charged growth sites of the growing crystals. The main practical AS suppression effects stem from the retardation of nucleation and crystal growth processes occurring in a supersaturated solution and the formation of distorted crystal structures of poor surface adherence capability [3,4].

Commonly used AS are derived from three chemical families: condensed poly(phosphate)s, organophosphates, and polyelectrolytes. Large quantities of polymeric scale inhibitors are frequently used for scale control in cooling water systems, desalination processes, and oil field operations. Like most conventional polymers, scale inhibitors are built for long existence and persist for many years after their disposal. Of particular concern are phosphorus-based inhibitors, which can serve as nutrients leading to eutrophication difficulties. Phosphorus and heavy metal discharges are regulated in many areas of the world, and permissible limits are decreasing.

Chemicals discharged into the marine environment have the potential for acute long-term effects on aquatic organisms. The magnitude of the impact depends on environmental and hydro-geological factors characteristic of the sea including bathymetry, waves, currents, and depth of the water column. Studies have identified several potential mechanisms by which chemical discharge may impact the marine ecosystems [5–7]. For example, a study [8] on the impact of continuous discharge of brine and power plant cooling water at the seashore of the Ashkelon SWRO plant (Israel) along with pulsed discharge of backwash water showed at the outfall increased salinity, temperature, and nutrient concentration levels, and reduced phytoplankton growth. It should be noted, however, that most of the published literature presents little or no empirical data to support statements regarding the environmental effects of desalination plants chemicals discharge [9].

Increasing environmental concern and discharge limitations brought about scale inhibitor chemistry to move towards green anti-scalants that readily biodegrade and have minimum environmental impact. A general product profile for ecologically benign inhibitor systems has been proposed by Schweinsberg et al. [10]: excellent scale inhibition, low aquatic and human toxicity, high biodegradability, good price/performance ratio, and free of phosphorus and nitrogen. In addition to these properties, a biodegradable scale inhibitor should prove that the desired biodegradability occurs after discharge; premature biodegradability before discharge would cause micro-organism contamination within the system. Currently, the most promising green scale inhibitors are based on polyaspartic acid (PASP), carboxymethyl inulin (CMI), and polycarboxylic acid [11].

One of the main factors hindering the practical application of biodegradable anti-scalants is the lack of reliable information on their performance from objective authoritative sources. In most studies of biodegradable anti-scalants by independent researchers [11], the inhibitory effectiveness was assessed by the rather crude "jar test technique" [12]. Inhibition effectiveness in this technique is evaluated by determining the percentage reduction in the mass of a scaling species precipitated over a day or so when the anti-scalant is added to a scaling supersaturated solution. The results of jar tests often correlate poorly with field performance [13].

The main objective of the current research is to advance the awareness of biodegradable anti-scalants by publication of reliable objective data based on more sophisticated evaluation techniques.

2. Experimental

2.1. Reverse osmosis system

The effectiveness of the tested anti-scalants was evaluated in a continuous flow membrane system (Fig. 1) equipped with a spiral wound RO module (FilmTec SW30 2521, Dow). The tests were conducted at a pressure of 20 bar, which provided an initial permeate flow rate of about 55 L/h. Concentrate flow rate was held constant at 500 L/h. The initial feed solution housed in a 200 L vessel simulated brackish water feed of an operating desalination plant prone to $CaCO_3$ scaling having the following composition: $Ca^{+2} = 105$, $HCO_3^- = 405$, $Mg^{2+} = 80$, $Na^+ = 365$, $SO_4^{2-} = 90$, $Cl^- = 650$, $SiO_2 = 27$, TDS = 1810 mg/L, and pH 7.2.

The inhibition effectiveness of an anti-scalant was determined by continuous withdrawal of permeate from the feed solution and recycling of the concentrate. The tested solution was thus subjected to a gradual concentration effect simulating the concentration effect experienced by a feed solution in a desalination process along the RO modules. The inhibition effectiveness was assessed by the water recovery level achieved before the onset of scaling [14]. The precipitation threshold was accurately determined from the abrupt changes in solution properties accompanying scale precipitation as described below.

2.2. Thermal system

Fig. 2 is a schematic diagram of the continuous flow system used to determine the effectiveness of green anti-scalants in alleviating $CaSO_4$ scale deposition on an electric element heating immersed in an agitated supersaturated solution operated at constant heat flux. The principle of the technique of scaling rate evaluation by constant flux heating is described in Section 3.2.

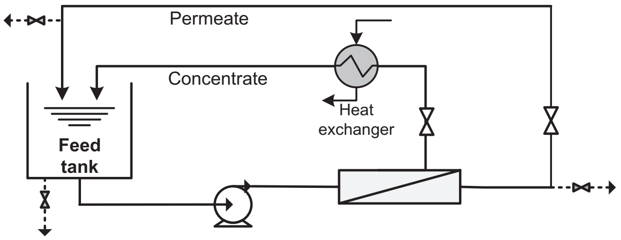

Fig. 1. Schematic description of the RO experimental system.

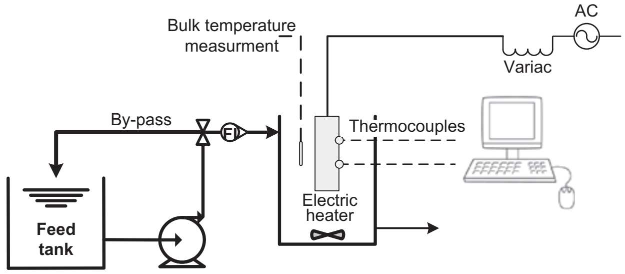

Fig. 2. Schematic diagram of the electrical heating system.

The electric heater, housed inside a 5 L agitated solution vessel, consisted of a cylindrical stainless steel element 2 cm diameter, 16 cm long, and 100 cm^2 surface area. The surface temperature of the electric heater was measured by two thermocouples embedded on the heater surface. Feed solution at a controlled composition of 0.045 mol/L $CaCl_2$ and 0.045 mol/L Na_2SO_4 was prepared in a 50 L tank and continuously fed to the solution vessel at a flow rate of 10 L/h. Rates of scale deposition on the electric heater were measured in a series of tests carried out in the presence of the anti-scalants at concentrations of either 1 or 2 mg/L and nominal heater surface temperatures of either 55 or 68 °C. The heater surface temperature was adjusted to the required surface temperature by regulating the voltage supplied to the electric heater using a variac. The power input supplied to the heater for maintaining a constant surface temperature of 55 °C was 202 W and for 68 °C, it was 332 W. The corresponding heat fluxes q/A were 17.3×10^3 and 28.5×10^3 kcal/h m^2 °C, respectively. The solution bulk temperature was about 40 °C in the 55 °C wall temperature runs and around 42 °C in the 68 °C runs.

The supersaturation driving force fostering the scaling process is represented by the saturation index, SI, given by:

$$SI = \frac{(Ca^{2+}) \cdot (SO_4^{2-})}{K_{sp}} \quad (1)$$

where, the bracketed terms are the ionic activities and K_{sp} is the equilibrium constant of gypsum. SI levels evaluated using Visual MinteQ Version 3 (2011) software were 2.84 at the surface temperature of 55 °C and 2.55 at the temperature of 68 °C. The lower SI level at the higher temperature is due to the inverse solubility of $CaSO_4$ in this temperature range.

2.3. Tested anti-scalants

The six commercial anti-scalants tested are here denoted by the alphabetical symbols A–F. Anti-scalants

A and B are so-called "unfriendly" anti-scalants, anti-scalant C is phosphorous free, while anti-scalants D, E, and F are considered to be green biodegradable anti-scalants. Anti-scalant A is a conventional, widely used phosphinocarboxylic acid polymer. Anti-scalant B is also a conventional, widely used, polyphosphonate-based polymer. Anti-scalant C is a maleic anhydride-acrylates copolymer free of phosphorous but not biodegradable. Anti-scalant D is a sodium salt of PASP. Anti-scalant E is a polycarboxylic acid-based polymer free of phosphorus, and anti-scalant F is a CMI polymer. Table 1 presents the biodegradation properties of anti-scalants D, E, and F as published by the manufacturers.

3. Results

3.1. Scale suppression results in the RO system

Assessment of the inhibition effectiveness of an anti-scalant by the water recovery level achieved before the onset of scaling was based on reliable identification of the start of the scaling process from changes in parameters induced by scaling, ie. permeate flux decline and changes in solution composition (pH, turbidity, calcium, and total alkalinity concentrations). Detection of scaling inception from permeability data is illustrated in Fig. 3 for duplicated runs 3 and 4 performed with 2 mg/L of AS-A. The sharp decline in the membrane permeability coefficient clearly denotes that the onset of scaling occurred at a water recovery level of 85%.

Figs. 4–7 illustrate determination of the onset of scaling with AS-D based on changes in solution composition properties. Fig. 4 shows that the pH level initially increases with increasing permeate withdrawal due to the increase in the carbonate concentration level. The abrupt decrease in the pH level, seen at water recovery levels of 75–80%, stems from the inception of $CaCO_3$ precipitation, which releases CO_2 acidity. Thus, the point at which the pH starts decreasing serves to detect the onset of scaling. Confirmation of this result is obtained by the turbidity data in Fig. 5, which display a sharp turning point at a water recovery level of 80%.

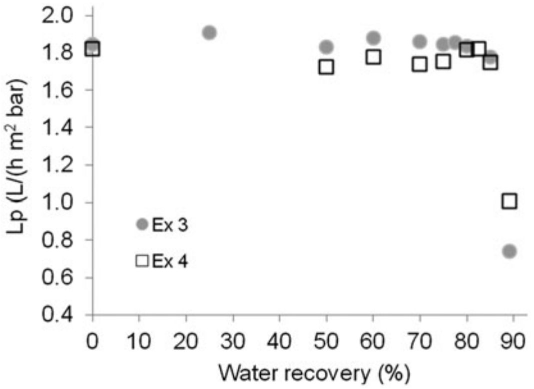

Fig. 3. Membrane permeability as a function of water recovery with 2 mg/L AS-A.

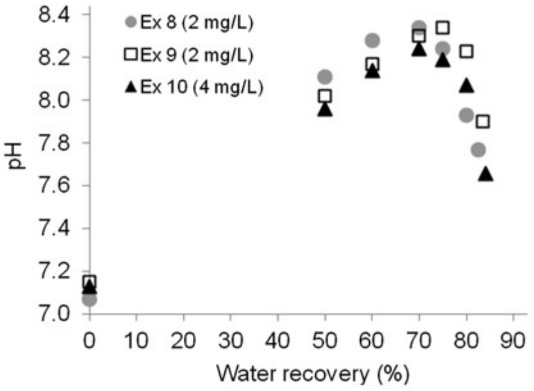

Fig. 4. Feed solution pH as a function of water recovery in the presence of 2 and 4 mg/L AS-D.

Fig. 6 illustrates detection of the onset of precipitation from the calcium content data. Precipitation is accompanied by depletion of calcium from the solution. However, since calcium concentration continually increases by the permeate withdrawal process,

Table 1
Biodegradation of anti-scalants D, E and F

Anti-scalant D	Anti-scalant E	Anti-scalant F
OECD-screening-test (modified) 301E: 74% anaerobic degradation: 30% after 56 d; ISO 11734 test	OECD 306 in 28 d (sea water conditions) and OECD 302b in 28 d (fresh water conditions): Readily biodegradable in salt water conditions and inherently biodegradable in fresh water conditions	Inherently biodegradable and non-toxic OECD 302A in 24 h > 20%

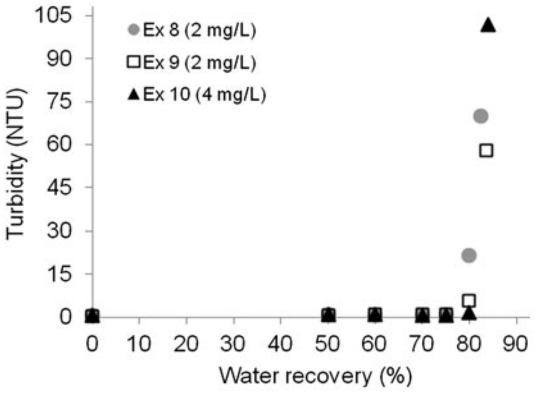

Fig. 5. Feed turbidity as a function of water recovery in the presence of 2 and 4 mg/L AS-D.

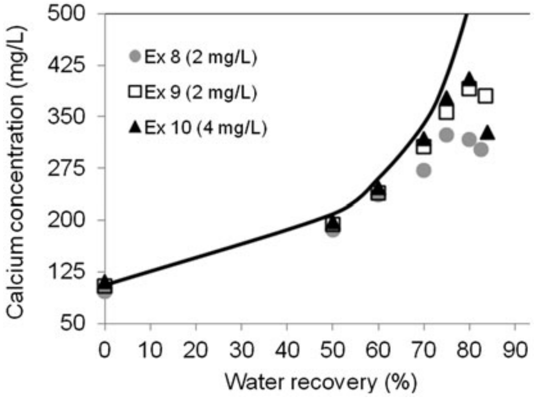

Fig. 6. Measured calcium concentrations (symbols) and theoretical “no precipitation” curve as a function of water recovery in the presence of 2 and 4 mg/L AS-D.

detection of the inception of precipitation is based on identification of the point at which the calcium concentration starts deviating from the value given by the following “no precipitation” concentration effect:

$$\mathrm{CF} = \frac{[\mathrm{Ca}]}{[\mathrm{Ca}]_o} = \frac{1 - [\mathrm{Ca}]_p \times Y}{1 - Y} \tag{2}$$

where, Y is the water recovery, CF is the concentration factor, $[\mathrm{Ca}]_o$ is the feed concentration, and $[\mathrm{Ca}]_p$ is the slight amount of calcium in the permeate.

Fig. 6 shows that the deviation points are at a water recovery level of 75% for dosage of 2 mg/L AS-D and 80% for dosage of 4 mg/L AS-D. These results are fully confirmed by a similar analysis of the carbonate alkalinity data shown in Fig. 7.

Table 2 displays data comparing the inhibition intensity of the tested anti-scalants. The location of precipitation, whether in the solution bulk and/or on membrane surface, is indicated. Inhibition effectiveness can be assessed by the extent of the water recovery and the Langelier Saturation Index (LSI) levels at the onset of scaling.

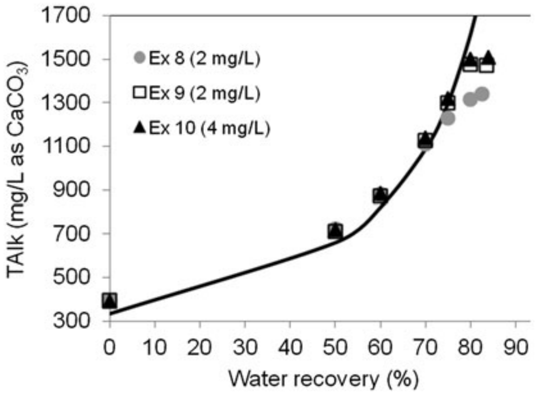

Fig. 7. Measured total alkalinity (symbols) and theoretical “no precipitation” curve as a function of water recovery in the presence of 2 and 4 mg/L AS-D.

The data in Table 2 show that the water recovery of the feed solution at the onset of precipitation was in the range of 70–85% in the presence of all tested anti-scalants compared with a water recovery of 60% in the absence of any AS. The conventional anti-scalants showed a slight advantage over the green anti-scalants at a dosage of 2 mg/L (80–85% water recovery with the conventional AS compared with 70–75% with the green AS). However, at a dosage of 4 mg/L, the performance of the green AS was essentially similar to that of conventional anti-scalants at a dosage of 2 mg/L.

Data emanating from anti-scalant suppliers indicate that prevention of $CaCO_3$ scaling is guided by application of an anti-scalant, which is able to maintain a scale-free solution at maximum LSI supersaturation levels in the range of 2.3–2.9 [15,16]. The LSI data in Table 2 show a slight advantage to the conventional anti-scalants but all green AS were able to maintain an LSI level within the recommended range of 2.3–2.9.

It may be concluded that the inhibitory effectiveness of the tested green AS was closely similar to that of the conventional AS.

3.2. *Scale inhibition results in the thermal system*

The inhibitory effectiveness of anti-scalants in scale deposition on a heated metal surface was evaluated from tests performed on a stainless steel electrical

Table 2
Data characterizing the $CaCO_3$ inhibition effectiveness of the tested anti-scalants

Anti-scalant	Dosage (mg/L)	Water recovery at onset of scaling (%)	Location of precipitate	Solution LSI	Membrane LSI
Control	0	60	Solution bulk	1.9–2.1	2.2–2.4
A	2	85	Membrane surface	3.0–3.1	3.3
B	2	80	Solution/membrane	2.9	3.1
C	2	73	Solution bulk	2.5	2.7
	4	80		2.7	3.0
D*	2	75	Solution bulk	2.4–2.6	2.7–2.8
	4	80		2.5	2.7
E*	2	75	Solution bulk	2.5–2.6	2.7–2.8
	4	80		2.8	3.1
F*	2	75	Solution/membrane	2.6	2.8
	4	80		2.9	3.1

*Green AS.

rod heated at a constant power input. A constant power input provides a constant heat flux q/A, where q is the heating rate and A is the heat transfer area. The advantage of this scale measurement technique is that the temperature at the solution-scale interface remains constant irrespective of the scale deposit thickness so that scale-layer growth rate is constant and layer thickness increases linearly with time. The increase in scale-layer growth can be conveniently determined by monitoring the metal surface temperature T_w. Analysis of the system [17] shows that the relation between scale layer thickness x and metal surface temperature is given by:

$$\frac{q}{A} = \frac{T_w - T_b}{\frac{x}{k_s} + \frac{1}{h}} = \text{Const.} \tag{3}$$

where, T_b is the solution bulk temperature, k_s is the thermal conductivity of the scale layer, and h is the heat transfer coefficient of the solution in contact with the scale deposit surface. Eq. (3) shows that at a constant heat flux q/A and a constant solution composition, both metal surface temperature, T_w, and scale thickness, x, increase linearly with time. The scale-layer growth rate $\mathrm{d}x/\mathrm{d}t$ can be simply determined from the slope of the line describing the linear growth of the surface temperature:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{A}{q} \cdot k_s \cdot \frac{\mathrm{d}T_w}{\mathrm{d}t} \tag{4}$$

The heat transfer coefficient (h) was obtained from the initial value of the surface temperature [$h = (q/A)/(T_s - T_b)$] and found to be 1,154 ± 138 kcal/h m^2℃ ($n = 17$). This is well within the typical range of 500–2,000 kcal/h m^2℃ of heat transfer coefficients in heated stirred vessels. The thermal conductivity (k_s) of the scale layer was evaluated from measurement of the final scale layer thickness and the final wall temperature (Eq. (3)), and found to be 0.59 ± 0.08 kcal/h m℃ ($n = 13$). This result is closely similar to the value of 0.5 kcal/h m℃ measured in a study of $CaSO_4$ scaling on a heated surface in the absence of anti-scalants [18].

Evaluation of the inhibition effectiveness of $CaSO_4$ scale deposition on a heated surface was based on the scale-layer growth rate level achieved in the presence of the various AS. Fig. 8 is a typical curve of the electric heater surface temperature with time. Two regimes can be distinguished—an induction regime in which an initial scale layer is forming on the heat transfer surface followed by a regime of scale-layer growth at a constant rate.

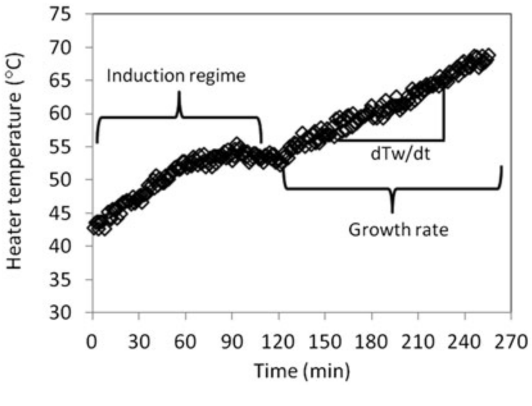

Fig. 8. Typical plot of the electric heater surface temperature versus time.

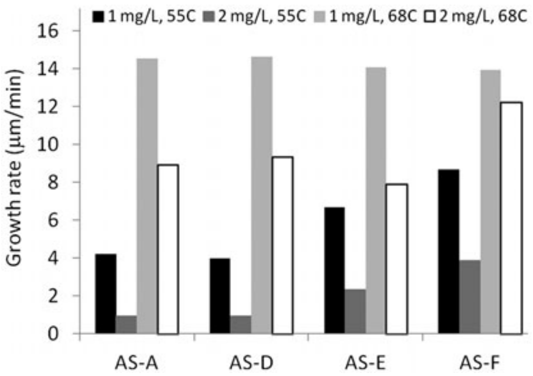

Fig. 9. $CaSO_4$ growth rate in the presence of 1 and 2 mg/L anti-scalants at electric heater temperatures of 55 and 68℃.

Fig. 9 compares the inhibition effectiveness of conventional anti-scalant A with that of the three green anti-scalants D, E, and F on the basis of the scale-layer growth rate level. At the lower scale surface temperature of 55℃, only the green AS-D, shows virtually identical scale inhibition effectiveness to that of the conventional AS-A. At the higher surface temperature of 68℃, the conventional and all the green anti-scalants show equally poor scale inhibition effectiveness.

4. Concluding remarks

This study, aiming to advance the awareness of green anti-scalants by publication of reliable objective data, showed that in the RO tests, $CaCO_3$ scale inhibition effectiveness of the three tested green anti-scalants closely approached that of conventional phosphonate-based anti-scalants. In $CaSO_4$ scale growth data measured on a heated metallic surface, only one of the three tested green anti-scalants closely approached the effectiveness of a conventional phosphonate-based anti-scalant. Overall, the data from both experimental systems indicate a promising potential for the already commercially available green anti-scalants and stress the need of further studies characterizing the inhibitory capabilities of green anti-scalants.

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