Inhibition by Poly(acrylic acid) and Morphological Changes in Calcium Carbonate and Calcium Carbonate/Calcium Sulfate Crystallization on Silica Fibers

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ABSTRACT: An intrinsic exposed core optical fiber sensor (IECOFS) made from fused silica was used to monitor the crystallization of calcium carbonate (CaCO₃) and CaCO₃/calcium sulfate (CaSO₄) composite at 100 and 120 °C in the absence and presence of low-molar-mass (Mₙ ≤ 2000) poly(acrylic acid) (PAA) with different end groups. The IECOFs responded only to deposition and growth processes on the fiber surface rather than changes occurring in the bulk of the solution. Hexyl isobutyrate-terminated PAA (Mₙ = 1400) and hexadecyl isobutyrate-terminated PAA (Mₙ = 1700) were the most effective species in preventing CaCO₃ deposition. Phase transformation from vaterite to aragonite/calcite decreased with increasing hydrophobicity of the PAA end group. Low-molar-mass PAA at 10 ppm showed very significant inhibition of CaCO₃/CaSO₄ composite formation for all end groups investigated.

INTRODUCTION

The economic production of fresh water from seawater has become an important goal worldwide due to increasing urbanization and industrial development in regions with limited ground and surface water resources. A critical factor contributing to the rapid uptake of seawater desalination technologies is the successful use of scale-control agents. Higher throughput requires working under higher brine concentrations and higher temperatures, conditions that favor the growth of scale-forming minerals. As a consequence, scale formation becomes the limiting factor in plant efficiency. The most important scale-forming minerals in desalination are calcium carbonate and magnesium hydroxide (at temperatures below about 100 °C) and calcium sulfate (at temperatures above about 100 °C), the latter usually occurring as a composite scale with Mg(OH)₂. In this work, inhibition of CaCO₃ and inhibition of the coprecipitation of CaSO₄ with CaCO₃ were investigated to complement previous studies by others.

In reverse-osmosis (RO) plants, scale formation on membrane surfaces not only reduces the rate of production and the quality of the fresh water product, but also accelerates degradation of the membranes. In thermal desalination plants, scale formation on surfaces reduces heat transfer and, hence, efficiency because of the lower thermal conductivity of the deposited material. The problem is usually managed by adding scale inhibitors in quantities in the parts-per-million range. These can be organic or inorganic compounds and either low-molar-mass compounds or polymers.

At present, the laboratory evaluation of scale inhibitors relies on instrumentation that measures changes in solution properties such as ion concentration (ion-selective electrodes), and the amount of small suspended particles (turbidity). However, there are difficulties in using these approaches at high temperatures and high concentrations. Turbidity measurements at high temperatures are limited by the formation of air bubbles, which interfere with those measurements, and are unreliable with highly turbid solutions. Ion-selective electrodes are fragile and costly, require long laboratory preparation times, and suffer from interference by related ions. Although scale deposition can be monitored by direct measurements of heat transfer across the surface, this method is difficult to implement on a laboratory scale.

Use of an intrinsic exposed core optical fiber sensor (IECOFS) is a cheap and portable method allowing real-time in situ measurement of scale formation on the laboratory scale. This method relies on the attenuation of laser light from an optical fiber as scale deposits on the surface. Such a sensor configuration has been demonstrated to be sensitive only to crystallization on the surface and not to phenomena farther than the order of the wavelength of light distant from the fiber surface, and the degree of attenuation was found to be approximately linear with the extent of surface coverage.

The optical fiber used in this study was made from fused silica, a high-refractive-index material (RI = 1.457), and because the solution has a lower RI, this results in internal reflection at the fiber/solution interface. As the RI of scale deposits is higher than the RI of the optical fiber core [1.58−1.68 for CaCO₃]
The fraction of light that is refracted outward increases as more scale is deposited on the optical fiber, so an optical fiber can be used to monitor scale deposition over time by recording the change in intensity of the laser light during the experiment.

The objective of the present study was to use an IECOFS to evaluate the surface crystallization of CaCO₃ and that of CaCO₃/CaSO₄ composite at 100 and 120 °C—the temperature range of interest for thermal desalination—and to determine the effectiveness of low-molar-mass poly(acrylic acid) (PAA, Mₐ < 2000) with different end groups in preventing scale crystallization under these conditions. We previously reported that changing the hydrophobicity of the end groups of low-molar-mass PAA can dramatically improve scale inhibition performance and change the speciation and morphology of both CaCO₃ and calcium oxalate crystals formed in the bulk, but in that work, we did not explicitly investigate the formation of scale on surfaces under conditions of interest for desalination in the presence of these PAA inhibitors.

Scaling on an unheated silica fiber cannot be expected to exactly duplicate scaling on heat-exchange surfaces: Although both metal and silica surfaces are hydrophilic and will be similarly adhesive toward CaCO₃ and CaSO₄, a heat-exchange surface will, on one hand, encourage turbulent mass transfer away from it and, on the other hand, generate bubbles that can act as nucleation sites.

### EXPERIMENTAL SECTION

**Optical Fiber System.** The IECOFS sensor developed in the authors’ laboratory for use at T ≥ 100 °C consists of a 5-mW He–Ne laser light source (λ = 632.9 nm, Uniphase, Milpitas, CA), temperature controller (Novus-N480D with a type J thermocouple), optical fiber cell, and photometric detector (Industrial Fiber Optics) (Figure 1). The optical fiber cell consists of a fiber core made of fused silica with a length of 21 cm (15 cm immersed in solution) and a diameter of 1.0 mm (F-MBE, Newport Corporation, Irvine, CA, and PUV-600T) with RI = 1.457 and a 70 mL cylindrical cell (borosilicate glass, 2.8 cm o.d. × 2.3 cm i.d. × 15 cm length) open on both sides. The cylindrical cell is sealed with O-rings against two nylon end plates. The end plates are fitted with stainless steel inserts machined to allow the optical fiber to pass through them and seal in place with locking screws and Teflon olives. The cell is surrounded by an aluminum block (4 cm × 4 cm × 14 cm) containing two 250-W elements for heating and a slot for viewing the turbidity of the solution.

Optical power attenuation (A) was calculated using the equation

\[ A = -\log_{10}\left(\frac{P_t}{P_0}\right) \]

where \(P_0\) and \(P_t\) are the intensities of light measured by the photometric detector at the initial time (\(t = 0\)) and at time \(t\), respectively.

The inhibition efficiency (IE, %) of PAA in reducing the heterogeneous crystallization of CaCO₃ on the optical fiber surface was determined by applying the equation

\[ \text{IE (%)} = \left(1 - \frac{A_{\text{PAA}}}{A_{\text{Blank}}}\right) \times 100 \]

where \(A_{\text{PAA}}\) is the final steady-state attenuation value in the presence of PAA and \(A_{\text{Blank}}\) is the final steady-state attenuation value in the absence of PAA (blank) under experimental conditions. Thus, the IE of PAA without any surface crystallization of CaCO₃ is 100%, and the IE of the blank is 0%.

**Synthesis and Characterization of Poly(acrylic acid).** A number of PAAAs with different end groups and molar masses were synthesized by atom-transfer radical polymerization (ATRP) of t-butyl acrylate, followed by hydrolysis of the resulting poly(t-butyl acrylate) by trifluoroacetic acid, as previously described. The PAA samples were characterized by \(^1\)H and \(^13\)C NMR spectroscopies (Bruker-300) and gel permeation chromatography (GPWaters 1525 HPLC, Waters autosampler 712 WISP and Waters 2414 RI detector).

The following low-molar-mass PAA samples were used (Figure 2): carboxymethyl-1,1-dimethyl-PAA [CMM-PAA, \(M_n\),...
for base hydrolysis of similar ethyl esters, which should, in turn, have a higher rate of base hydrolysis than the other esters prepared.18

In the second phase of the experimental work, the coprecipitation of CaCO3 and CaSO4 was investigated. Three solutions, 0.5 M (48000 ppm) SO4−2 as Na2SO4, 0.0625 M (3750 ppm) CO3−2 as Na2CO3, and 0.15 M (6000 ppm) Ca2+ as CaCl2 were prepared. These solutions and the RO water used were filtered and degassed using a 0.45-μm Millipore solvent filter. Deionized water (48 mL, filtered using a 0.45-μm cellulose acetate membrane) was added to the Na2SO4 solution to give a final concentration of 5760 ppm in the absence and presence of 6.7 ppm PAA and was then placed in a 70 mL cleaned cell with magnetic stirring. When the solution reached the target temperature (120 °C), 1 mL of CO3−2 as Na2CO3 solution and 1 mL of Ca2+ as CaCl2 solution were added to the cell to give final concentrations of 75 and 120 ppm, respectively [Qp/Kp (CaCO3) = 2752, where Qp is the ion product reaction quotient and Kp is the solubility product constant] and a pH of 9.0.

Recording of the reduction in the laser light density was begun immediately upon the injection of the calcium and carbonate solutions and detected by photometric detector for 1000 s. Analog outputs from the photometric detector were digitally converted using a Picolog A/D Converter 16 (16 bit) and Picolog recording software, and data were acquired every 30 s.

Scanning Electron Microscopy. Optical fiber samples from the experiments in the absence and presence of PAA (Mn ≤ 2000) were collected at the end of the experiments (after 1000 s) and characterized by scanning electron microscopy (SEM). These samples were gold-coated, and the SEM images were obtained using a FEI Quanta 200 Environmental SEM instrument at an accelerating voltage of 15 kV in the electron microscopy facility of Queensland University of Technology. Elemental composition was determined by electron-dispersive spectroscopy (EDS) using a JEOL JXA-840 instrument (20 kV, 1.0 nA, T3) and JEOL Analysis Program (v3.30).

RESULTS AND DISCUSSION

Calcium Carbonate: Crystallization on Optical Fiber Surface at 100 °C. In the absence of any scale inhibitor, a linear attenuation response (R2 = 0.995, n = 18) of the IECOFS sensor was obtained over the first 510 s of measurement.

Figure 2. Poly(acrylic acid) end groups investigated.
(Figure 2), consistent with previous reports on the formation of CaCO3 at 25 °C.10 The results indicate continuing heterogeneous crystallization on the optical fiber surface with an overall attenuation rate of 0.0026 s⁻¹. The attenuation rate then gradually reduced, reaching an apparent steady state near the end of the experiment (Figure 3). In a previous work, we demonstrated that this attenuation profile corresponds to linear growth in terms of the average thickness of a layer of deposited

Table 1. Inhibition Time (IT), Initial Attenuation Rate, and Final Attenuation for the Crystallization of CaCO3 on Optical Fiber Surface in the Presence of PAA

<table>
<thead>
<tr>
<th>end-group-terminated PAA</th>
<th>$M_n$</th>
<th>IT (s)</th>
<th>maximum rate of attenuation ($\times 10^{-4}$ s⁻¹)</th>
<th>final attenuation</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>~</td>
<td>0</td>
<td>27 ± 3</td>
<td>1.48 ± 0.11</td>
</tr>
<tr>
<td>hydrophilic end group</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CMM</td>
<td>2106</td>
<td>19</td>
<td>39 ± 15</td>
<td>0.530 ± 0.022</td>
</tr>
<tr>
<td>hydrophobic end groups</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EIB</td>
<td>1669</td>
<td>19</td>
<td>23 ± 6</td>
<td>0.534 ± 0.029</td>
</tr>
<tr>
<td>CIB</td>
<td>1689</td>
<td>72</td>
<td>21 ± 16</td>
<td>0.477 ± 0.025</td>
</tr>
<tr>
<td>HIB</td>
<td>1403</td>
<td>&gt;360</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HDIB</td>
<td>1687</td>
<td>&gt;360</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 4. Attenuation of the IECOFS signal with and without PAA ($M_n \leq 2000$) with different end groups: (⧫) blank, (×) CMM, (▲) EIB, (●) CIB.

Figure 5. SEM images of CaCO3 crystals on optical fiber surfaces (diameter = 1000 μm) prepared in the absence of PAA at 100 °C: (a) 200000x magnification showing CaCO3 as a rodlike polymorph, (b) 1000000x magnification showing CaCO3 as a rhombohedral calcite polymorph.

Figure 6. (a) Experimental morphology of aragonite20,21 and (b) equilibrium morphology of hydrated calcite.19 Adapted with permission from ref 19. Copyright 1998 American Chemical Society. Darker shading indicates higher surface energy.
High turbidity was seen in the bulk solution for the blank, and a medium amount of turbidity was seen for HDIB-PAA, but only low turbidity was observed in the presence of CMM-PAA, EIB-PAA, and CIB-PAA, and no visible cloudiness was observed with HIB-PAA. Precipitation on the walls of the tube cell was again high for the blank and low for most of the PAA samples, but both HIB-PAA and HDIB-PAA gave no observable precipitation (Table 1). Quantitative attenuation results from the same experiments obtained with the IECOFS are given in Figure 4.

In contrast to the linear IECOFS attenuation that was obtained in the absence of PAA, in the presence of PAA, a

Figure 7. SEM images of crystallization of CaCO$_3$ on an optical fiber core (diameter = 1.0 mm) in the presence of 6.7 ppm CIB-PAA at 100 °C: (a) 2000× and (b) 30000× magnification, showing highly distorted vaterite florettes.

Figure 8. (a) Equilibrium morphology of hydrated vaterite as determined from atomistic simulations, where darker shading indicates higher surface energy, and (b) stylized representation of the vaterite florette morphology observed experimentally.

Figure 9. SEM images of heterogeneous crystallization of CaCO$_3$ on an optical fiber core (diameter = 1.0 mm) in the presence of 6.7 ppm EIB-PAA at 100 °C: (A) 2000× and (B) 15000× magnification showing a mixture of three polymorphs of CaCO$_3$ (vaterite, rodlike aragonite, and rhombohedral calcite).

Figure 10. SEM image (50000×) showing a distorted rhombohedral calcite polymorph on an optical fiber core (diameter = 1.0 mm) in the presence of 6.7 ppm CMM-PAA at 100 °C.
heat-transfer tubes. For example, at the Al-Jubail multistage time is less than 5 min, so an IT greater than this would be desirable. The conditions used in this study maintain a Ca2+/CO32- ratio of >1 and a high supersaturation of the same order, (ii) the rate of change during the period of rapid change, and (iii) the final level of attenuation achieved (Table 1). These three parameters address different stages of the crystallization process.

Inhibition time (IT), a measure of the time before the onset of detectable crystallization, was measured from the intercept of the attenuation curve with the x axis. In the presence of PAAs with hydrophilic (CMM) and short hydrophobic (EIB) end groups, the IT was short (19 s). However, in the presence of a PAA with an intermediate-length hydrophobic end group (CIB), the formation of CaCO3 in the optical fiber surface did not begin until after a 72-s IT as shown in Figure 4.

The required inhibition time for thermal desalination depends on the brine recycle flow and the diameter of the heat-transfer tubes. For example, at the Al-Jubail multistage flash (MSF) desalination plant in Saudi Arabia, the retention time is less than 5 min, so an IT greater than this would be desirable. The conditions used in this study maintain a Ca2+/CO32- ratio of >1 and a high supersaturation of the same order as thermal desalination plant operating conditions, but the IT values measured here are not directly applicable to plant operating conditions. The conditions used in this study were designed to force faster scale formation than is seen under plant operating conditions, where it can take several days before any scaling is observed, and are the conditions used for evaluating scale inhibitors at the Saline Water Desalination Research Institute (SWDRI, Al-Jubail, Saudi Arabia). (It should be noted that a low IT is also not necessarily required for improvement in performance, if a scale control agent is capable of giving a good steady-state inhibition efficiency.)

The maximum attenuation rate was obtained from the slope of the plots of attenuation as a function of time (Figure 4). No significant difference in attenuation rates was observed between experiments carried out in the absence (blank, $A = 0.0027 \text{ s}^{-1}$) and presence of PAA with hydrophobic end groups (EIB, 0.0023 s$^{-1}$; CIB, 0.0021 s$^{-1}$). However, the attenuation rate in the presence of PAA with hydrophilic end groups (CMM, 0.0039 s$^{-1}$) was higher than that of the blank, as shown in Table 1 and Figure 4. This suggests that, under these conditions of approximately equimolar cation and anion concentrations, there might be a difference in the mechanism of action between PAA terminated by hydrophobic end groups and the other PAAs investigated in this work.

The final steady-state attenuation is the value obtained after the linear growth when the curve leveled off. This is most likely related to the ability of the PAA to stabilize crystals in the bulk, so that they do not affect the IECOFS, as can be seen from the turbidity qualitatively observed with HDIB-PAA. The rate of attenuation in each case appears to approach a steady-state value, with lower attenuation values obtained at the end of the experiment for more hydrophobic PAA end groups.

In agreement with the qualitative observations, HIB-PAA and HDIB-PAA, where no precipitation was seen on the heat-transfer tube, also gave no attenuation of the optical fiber signal over the time scale of the experiment.

**Calcium Carbonate Crystal Morphology.** Scanning electron micrographs of the optical fiber surface in the absence of PAA after 1000 s of crystallization showed crystals of CaCO3 occurring primarily in a rodlike morphology with an average crystal length of 8 μm and with some single crystals of rhombohedral calcite (Figure 5). The rodlike morphology is most likely to consist originally of aragonite growing with the longest crystal axis displaying a {110} twinning crystal plane.

The calculated morphologies of hydrated aragonite and calcite are shown in Figure 6. At equilibrium, faces with lower surface energies will be favored and exposed. The surface energies calculated from atomistic simulations of hydrated CaCO3 are qualitatively represented in Figure 6, where darker shading on a face represents a higher calculated surface energy. The surface energies represented are averages of the...
values calculated for the Ca$^{2+}$- and CO$_3^{2-}$-terminated faces, which was judged to be appropriate for the approximately 1:1 cation-to-anion ratio conditions used in this study.

Scanning electron micrographs obtained in the presence of PAA with a midlength hydrophobic end group (CIB) showed crystals of CaCO$_3$ present as the vaterite polymorph (Figure 7). The images with CIB-PAA also illustrated the highest distortion

Table 2. Inhibition Efficiency of PAA with Different End Groups in Preventing Surface Crystallization (SC) and Bulk Crystallization (BC) of CaCO$_3$

<table>
<thead>
<tr>
<th>end group</th>
<th>$M_n$</th>
<th>SC (%)</th>
<th>BC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td></td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>hydrophilic end group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CMM</td>
<td>2106</td>
<td>64.3</td>
<td>65.9</td>
</tr>
<tr>
<td>hydrophobic end groups</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EIB</td>
<td>1669</td>
<td>64.0</td>
<td>75.0</td>
</tr>
<tr>
<td>CIB</td>
<td>1689</td>
<td>67.9</td>
<td>93.0</td>
</tr>
<tr>
<td>HIB</td>
<td>1403</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>HDIB</td>
<td>1687</td>
<td>100.0</td>
<td>45.5</td>
</tr>
</tbody>
</table>

Figure 13. Attenuation of the IECOFS signals in three different experiments (red, green, blue) in the absence of PAA (blank) with progressive cocrystallization of CaCO$_3$ and CaSO$_4$ at 120 °C. (Black is the average.)

Figure 14. SEM micrograph of an exposed optical fiber core (diameter = 1000 μm) in the absence of PAA (blank) for the coprecipitation of CaCO$_3$ and CaSO$_4$ at 120 °C: (a) 250× magnification showing a section of an exposed optical fiber core, (b) 2500× magnification showing crystals of CaCO$_3$ and CaSO$_4$. 

in the floral vaterite polymorph, which might be due to stronger adsorption of CIB-PAA on active faces or edges of the growing vaterite nuclei. In a previous study of bulk crystallization, we found highly distorted vaterite, calcite, and aragonite in the presence of PAA with midlength hydrophobic groups.15 Figure 8a shows the equilibrium morphology of hydrated vaterite crystals as determined by atomistic simulation.19 Calculated surface energies predict that the Ca$^{2+}$-terminated {010}, CO$_3^{2-}$-terminated {011}, and Ca$^{2+}$-terminated {101} faces are the most energetically stable, and the disklike morphology seen is similar to the observed experimental morphologies (Figure 8b).20

In the presence of PAA with short hydrophobic end groups (EIB), crystals of CaCO$_3$ occurred primarily as a mixture of distorted vaterite florettes with a few rodlike crystals and trace of rhombohedral calcite, as shown in Figure 9. However, the SEM micrograph of CaCO$_3$ crystals in the presence of PAA with hydrophilic end group (CMM) exhibited a distorted rhombohedral calcite, as shown in Figure 10, consistent with previous observations of crystallization in the bulk in the presence of CMM-PAA.15 The distortion in rhombohedral calcite might be due to the adsorption of CMM-PAA on the positively charged face {1010}, which is the fastest growing face in the crystal of rhombohedral calcite, and the neutral face {1010}.22

As the hydrophobicity increased with increasing length of the end groups on PAA, the amount of the less thermodynamically stable vaterite polymorph increased (Scheme 1). Ostwald’s rule of stages suggests that the thermodynamically least stable vaterite is formed first, with the calcite formed by dissolution and reprecipitation of vaterite,23 and this is consistent with previous reports of the effect of PAA on CaCO$_3$ crystallization.24 It has been reported that CaCO$_3$ forms through an initial amorphous phase,25 giving the temporal mapping of CaCO$_3$ formation in the presence of PAA shown in Figure 11.

Note that the initially formed structure of hydrated vaterite has relatively low surface attachment energies, with greater values estimated for the final rodlike aragonite polymorph, consistent with Ostwald’s rule. The more flattened aragonite morphologies seen in the presence of PAA (Figure 9) in comparison to those observed in the absence of PAA (Figure 5) suggest that growth of the {110} face with a relatively low attachment energy is inhibited by the adsorption of PAA.
Calcium Carbonate Inhibition Efficiency. PAA with HIB and HDIB hydrophobic end groups fully retarded surface precipitation under the experimental conditions, with no significant change in attenuation of the IECOFS obtained. Those results were reinforced by SEM micrographs of optical fiber core samples in the presence of HIB-PAA and HDIB-PAA, which showed no visible crystals (Figure 12). Although there was significant crystallization of CaCO₃ in the bulk solution in the presence of HDIB-PAA, the surface of the optical fiber and heat-transfer tube were clean. These results are good evidence that the IECOFS is responsive to only surface crystallization.⁹,¹⁰ The significant difference in the efficiency of HDIB-PAA in inhibiting CaCO₃ crystallization in the bulk solution and the surface can be explained by its higher surface activity, as it is the polymer with the greatest ratio of hydrophobic end groups to hydrophilic chains. This phenomenon was evident from the large amounts of foam previously observed when solutions containing 10 and 15 ppm of this material were boiled.⁶ This interfacial activity is likely to lead to self-assembly of HDIB-PAA in the bulk, providing additional nuclei for the deposition of calcium carbonate in competition with heterogeneous crystallization on the fiber surface. Alternatively, the larger hydrophobic domain might be better able to associate with relatively uncharged areas on forming crystals, enhancing the role of HDIB-PAA as a dispersant.

Energy-dispersive X-ray spectroscopy (EDS) of the light spots appearing in the SEM images of fibers obtained in experiments with HIB-PAA and HDIB-PAA (Figure 11) found only Si and O, suggesting that they are silica artifacts of sample preparation.

The inhibition efficiency of PAA with different end groups to prevent surface crystallization of CaCO₃ in order of decreasing percentage IE was HIB > CIB > EIB > CMM, which was the same order as found previously for crystallization in bulk solution (Table 2).¹⁵ We provisionally attributed this trend, where hydrophobic end groups provide improved inhibition up to a certain size of end group, to selective adsorption at the edges between faces of different charge densities. It is reasonable that a hydrophobic group should direct adsorption to an edge between a more highly charged and a less highly charged face, giving better inhibition of growth and a greater tendency to retard crystals in a kinetically favored polymorph. We are currently carrying out molecular dynamics calculations to test this hypothesis.

The inhibition efficiency of HDIB-PAA is significantly different in this system than previously found during an investigation of bulk crystallization, with IEs of 100% and 45% for the surface and bulk crystallization, respectively, of CaCO₃. This strongly suggests that the deposition of crystals on the fiber surface is a two-stage process. The predominant mechanism for the inhibition of CaCO₃ formation in bulk solution is most likely through the adsorption of PAA onto the active faces of CaCO₃ crystals, but PAA can also act as a dispersant and prevent the adsorption of CaCO₃ crystals onto the fiber surface: It is reasonable that this dispersing effect would be most significant for the PAA with the most hydrophobic end groups. The structural factors leading to efficient inhibition by these two mechanisms are not the same and point to different strategies for optimal PAA scale inhibitor design.

Calcium Carbonate and Calcium Sulfate: Crystallization on Optical Fiber Surface at 120 °C. Attenuation of the IECOFS signal in solutions containing 5760 ppm SO₄²⁻ as Na₂SO₄ 75 ppm CO₃²⁻ as Na₂CO₃, and 120 ppm Ca²⁺ as CaCl₂ and in the absence and presence of 6.7 ppm PAA (Mₑ ≤ 2000 g/mol) with different end groups at pH 9.0 and T = 120 °C was determined over 50 min.

No induction period was observed in the absence of PAA. A linear response of the attenuation signal from the IECOFS was obtained in the absence of PAA for the period of 0–260 s (Figure 13). In that period, the overall attenuation rate was 0.0039 ± 0.0004 s⁻¹, indicating steady heterogeneous crystallization on the optical fiber surface. After that period, the change in attenuation slowed until the system reached a steady state. At the end of each experiment, a large amount of precipitate was observed on the surface of the heat-transfer tubes. This was largely loose material that was presumably generated by crystallization in the bulk phase and precipitated on the surfaces.

Under the same experimental conditions, the change in attenuation for precipitation of CaSO₄ was very slow, although precipitation was observed in the bulk solution. This might indicate that the kinetics of heterogeneous deposition of CaSO₄ are very slow or that it is only weakly adherent on the optical fiber surface. Therefore, the predominant deposit in the first period of the heterogeneous coprecipitation of CaCO₃ and CaSO₄ is likely to be CaCO₃, which forms more rapidly and gives more adherent deposits than CaSO₄; by itself, CaSO₄ does not usually form an adherent scale, but is increasingly tenacious with a higher admixture of CaCO₃. Initial formation of CaCO₃, which then bonds the CaSO₄ deposit layer, was proposed to occur on a heated stainless steel surface by Bramson et al.²⁶

In contrast to previous observations of Sheikholeslami and Ng, carried out at 60–70 °C in a solution with an excess of SO₄²⁻, a dominant needlelike polymorph of CaSO₄·2H₂O was not observed on the optical fiber surfaces.³ SEM micrographs of the optical fiber surfaces (Figures 14 and 15) instead showed clusters that are consistent with distorted calcite and vaterite structures of CaCO₃ with some CaCO₃ as a rodlike hexagonal calcite and single crystals apparently of rhombohedral calcite. This is despite the fact that the excess of sulfate over carbonate species employed in this work (48:1) was greater than that used by Sheikholeslami and Ng (14–2:1),² below and it is proposed that CaSO₄ was generated in the bulk phase and was not adherent.

The dominant polymorph of CaCO₃ crystals observed on the fiber surface was affected by the presence of CaSO₄ as the rodlike aragonite polymorph of CaCO₃ seen in the precipitation of CaCO₃ (Figure 5) was replaced by hexagonal calcite clusters in the coprecipitation. This result is in agreement with the observation of Sudmalis and Sheikholeslami that the presence of one scale-forming mineral can affect the structure of the other in the coprecipitation of CaCO₃ and CaSO₄, although, in other respects, these results are dissimilar to theirs.² It is possible that the interpenetrating platelike crystals seen in Figure 15c are CaSO₄ as similar structures were attributed to CaSO₄ in images of coprecipitates of CaCO₃ and CaSO₄ imaged by Sudmalis and Sheikholeslami,² but these structures were not common in the precipitate on the surface. It has been reported that the incorporation of small amounts of sulfate is energetically favorable in the vaterite structure, unfavorable in calcite, and very unfavorable in aragonite,²⁷ which might explain the dominance of distorted vaterite and calcite structures in these precipitates over aragonite, the dominant species seen in the precipitation of CaCO₃ in the absence of inhibitor.
CONCLUSIONS

The heterogeneous precipitation of CaCO₃ and the coprecipitation of CaCO₃ and CaSO₄ at 100–120 °C were studied using an intrinsic exposed core optical fiber sensor (IECOFS). The effect of PAA samples (Mₙ ≤ 2000) with different end groups on the heterogeneous precipitation of CaCO₃ at 100 °C was found to be significant. The results confirmed previous observations that the end groups of PAA play very important roles, with PAA containing midlength (HIB) and long (HDIB) hydrophobic groups having an excellent inhibition efficiency to prevent the heterogeneous deposition of CaCO₃. Moreover, the results for PAA samples with short hydrophilic (CMM) and hydrophobic (EIB) and intermediate-length hydrophobic (CIB) end groups showed that the inhibition efficiency increased with increasing hydrophobicity of the end group. Microscopic examination of the deposits on the optical fibers confirmed that the more effective the PAA in inhibition, the more ill-formed the CaCO₃ crystals and the more likely they were to be of the kinetically favored vaterite polymorph rather than the thermodynamically favored calcite polymorph.

These results are consistent with a model in which the hydrophobic end groups directly adsorb to the scale inhibitors preferentially to the edges between highly charged and near-neutral faces, giving better control of growth than adsorption onto faces of the forming crystallites.

Low-molar-mass PAA with a long hydrophobic end group (HDIB) showed different inhibition efficiencies for crystallization in the bulk and on the optical fiber surface, which might be due to the inhibition of precipitation on the optical fiber surface by stabilization of crystals in the bulk phase, as well as inhibition of crystal nucleation and growth, or by competition with the surface in providing additional sites for crystal nucleation.

The results for the inhibition efficiency of PAA samples with different end groups to prevent the heterogeneous coprecipitation of CaCO₃ and CaSO₄ at 120 °C showed an excellent inhibition efficiency for 10 ppm PAA with all end groups investigated, making it impossible to differentiate between their levels of effectiveness.

The IECOFS demonstrated a number of advantages over conventional methods for monitoring scale precipitation. First, the IECOFS response is only for heterogeneous crystallization on the surface of the fiber. Second, the IECOFS can readily be used at the high temperatures and ionic strengths relevant to the conditions important for the thermal desalination of seawater. Third, used IECOFS fibers are easily susceptible to further analysis to probe crystallization phenomena in detail.

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Notes
The authors declare no competing financial interest.

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