Novel Monitors Enable Early Detection of RO System Fouling

Thermal Systems

- Humidification–Dehumidification Design Aids Small-Scale Systems
- New Antiscalant Offers Improved Biodegradability and Bioaccumulation

Energy

- Continuous Closed-Circuit Desalination Process Improves Energy Consumption
- New Method Recovers Osmotic Power
Antiscalants are applied in thermal desalination plants (multistage flash and multieffect desalination) to control alkaline and nonalkaline scale in brine when saturation indices are exceeded. Antiscalants currently used are usually based on organophosphonates or are polymeric in nature. These antiscalants are discharged into the sea via brine blowdown and remain in the environment for a long time. Some of these antiscalants bioaccumulate in living organisms or act as a food source for microbes. Data presented in this article show the biodegradability and bioaccumulation properties of a new phosphorus- and nitrogen-free antiscalant. Performance data show the new antiscalant controls scale in brines up to a concentration factor of 2 and temperatures to 120°C. Saturation indices of these brines were calculated and correlated with the dose level required to control scale deposition. In addition, a detection method has been developed to help thermal plant operators measure antiscalant in brine, allowing them to control the dosage level.

A New Biodegradable Antiscalant for Thermal Desalination Plants

Suresh Patel

Thermal desalination plants are based on multistage flash (MSF) or multieffect desalination (MED) processes in which seawater is heated so that the pure water evaporates, resulting in distillate and the remaining brine being removed via the blowdown (Buros, 1980; Forrester, 1975). During this process, brine concentration increases. The concentration of dissolved salts in the brine also increases and eventually leads to exceeding the solubility limits (or supersaturation) of the salts, resulting in the precipitation of alkaline (calcium carbonate and magnesium hydroxide) and nonalkaline (calcium sulfate) salts, depending on brine chemistry and temperature.

This article presents several methods (Langelier, 1936; Stiff and Davis, 1952; Ryznar, 1944; Larson and Skold, 1958) for determining supersaturation of brine by calculating the saturation index of individual salts. The author used the following equations:

Equation 1: Calcium carbonate
\[ SI_{\text{CaCO}_3} = \frac{[\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}]}{K_{\text{spCaCO}_3}} \]

Where:
- \( SI_{\text{CaCO}_3} \) = saturation index for calcium carbonate
- \([\text{Ca}^{2+}]\) = concentration of calcium ions
- \([\text{CO}_3^{2-}]\) = concentration of carbonate ions
- \( K_{\text{spCaCO}_3} \) = solubility product for calcium carbonate

Equation 2: Magnesium hydroxide
\[ SI_{\text{Mg(OH)}_2} = \frac{[\text{Mg}^{2+}] \cdot [\text{OH}^-]}{K_{\text{spMg(OH)}_2}} \]

Where:
- \( SI_{\text{Mg(OH)}_2} \) = saturation index for magnesium hydroxide
- \([\text{Mg}^{2+}]\) = concentration of magnesium ions
- \([\text{OH}^-]\) = concentration of hydroxyl ions
- \( K_{\text{spMg(OH)}_2} \) = solubility product for magnesium hydroxide

Equation 3: Calcium sulfate
\[ SI_{\text{CaSO}_4} = \frac{[\text{Ca}^{2+}] \cdot [\text{SO}_4^{2-}]}{K_{\text{spCaSO}_4}} \]

Where:
- \( SI_{\text{CaSO}_4} \) = saturation index for calcium sulfate
- \([\text{Ca}^{2+}]\) = concentration of calcium ions
- \([\text{SO}_4^{2-}]\) = concentration of sulfate ions
- \( K_{\text{spCaSO}_4} \) = solubility product for calcium sulphate

These saturation indices were calculated using a commercial software program (Ferguson, 1991).

Scale deposition can occur on heat exchanger surfaces, demisters, pipe work, stage or cell walls and floors, and in brine, which results in production losses and increases maintenance costs resulting from down time, extra cleaning chemicals, or ultimately replacement parts.

Thermal desalination plant operators currently use antiscalants that are based on organophosphonates or are polymers based on maleic-acid or acrylic-acid chemistry to control typical scaling. Usually used in low-temperature plants to control calcium carbonate, organophosphonates poorly control calcium sulfate (Caplan, 1998; Cody, 1991), and, if used at high temperatures, breakdown to orthophosphate, which leads to calcium phosphate formation.
In addition, organophosphonates are not capable of dispersing scales or silt that may be present in raw seawater. Polymeric antisalant chemistry varies from simple polyacrylic or polymaleic types to complex polycarboxylic containing different monomers. The most successful type of polymeric antisalant is based on polyacrylic chemistry\(^2\) used in the late 1960s to the mid-1990s (Finan et al., 1989). From the mid-1990s to date, enhanced maleates\(^3\) have been used. These polymeric antisalants have significant advantages over organophosphates, because they provide multifunction scale-control properties for scaling found in thermal desalination plants (Patel and Finan, 1999).

Antisalants currently being used in thermal desalination plants are discharged via brine blowdown and, at most sites, into the seawater. The antisalants remain in the sea or in sludge form by adsorbing onto silt and sand. Antisalants used in thermal desalination plants are not biodegradable, but they will break down over time and remain in the environment for a long time (Hoepner and Latteman, 2002).

In addition, antisalants containing phosphorus and nitrogen can be food sources to bacteria and algae and can lead to eutrophication (Smith et al., 1991). Therefore, antisalants with or without low levels of phosphorus and nitrogen would minimize eutrophication in seawater.

Determining the amount of antisalant being dosed into the seawater feedline is a challenge, especially at sites where a centralized dosing tank distributes the correct dose level of antisalant to individual distillers. Although such inconsistent dosing has led to scale formation in distillers, this has only been observed when distiller performance deteriorates over a period of operation or when the distiller is opened for inspection. Therefore, if antisalants can be monitored in the seawater feed, as well as the concentrated brine, the amount of antisalant present can be confirmed.

This study evaluated a new antisalant\(^4\) (Antiscalant A) that does not contain phosphorus or nitrogen, is biodegradable, and will not remain in the marine environment for a long time. The objective was to find a fast, easy-to-use, accurate way to determine, control, and maintain antisalant dose level to control scale deposition and provide for efficient distiller operation.

**Experimental Results**

**Composition of New Antiscalant.** A specialty chemicals company\(^5\) developed Antiscalant A, which is based on polycarboxylic acid chemistry (phosphorus and nitrogen free).

**Biodegradation Study.** A study of Antiscalant A’s aerobic biodegradation in seawater was carried out using the Organisation for Economic Co-operation and Development (OECD) 306 procedure (OECD, 1992). Used successfully in the oil industry, these tests were carried out by an external testing house certified to Good Laboratory Practice (GLP) status. Antiscalant A was assessed for biodegradation rate and extent when exposed for 28 days to marine micro-organisms. The results were compared with sodium acetate, a standard that biodegrades in this test. The test measured the dissolved organic carbon (DOC) at 0, 7, 14, 21, and 28 days.

Natural seawater was collected from Penrhyn Point, North Wales. At the time of collection, the seawater was 12°C and had pH of 8.13, salinity of 29.8 g/L, and dissolved oxygen (DO) content of 96.3 percent. After collection, the seawater was coarse-filtered and maintained in the dark.

As expected, the standard used—sodium acetate—biodegraded rapidly, which confirmed the test’s validity. Figure 1 shows that, within 28 days, Antiscalant A is more than 60 percent biodegradable in the OECD 306 test and can be classified as biodegradable.

Biodegradability of typical, currently used antisalant chemistries are shown in Table 1, which illustrates that sodium polyacrylate (FloTtec, 2009) and phosphonate 1 and phosphonate 2 chemistries are not biodegradable.

**Bioaccumulation Study.** Antiscalant A’s potential to bioaccumulate was assessed in n-octanol, and water partition was measured using OECD method 117 (OECD, 1989), which determines the n-octanol–water partition coefficient

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Table 1. Biodegradation results for antisalant chemistries in OECD 306 test

<table>
<thead>
<tr>
<th>Product</th>
<th>Biodegradability at 28 days, %</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antiscalant A</td>
<td>68.6</td>
<td>Biodegradable</td>
</tr>
<tr>
<td>Na-PA</td>
<td>2.7</td>
<td>Not biodegradable</td>
</tr>
<tr>
<td>Phosphonate 1</td>
<td>0</td>
<td>Not biodegradable</td>
</tr>
<tr>
<td>Phosphonate 2</td>
<td>6.6</td>
<td>Not biodegradable</td>
</tr>
</tbody>
</table>
Thermal Technologies

Figure 2. High-temperature tube-blocking equipment

Figure 3. Scale deposition at various temperatures in a brine at a 1.5 concentration factor

(log pow). If the value is more than 3, an antiscalant will bioaccumulate. Antiscalant A’s log pow was 0.73, indicating a low bioaccumulation potential. Therefore, there is no possibility that Antiscalant A will bioaccumulate in any food chain.

Determining Scale Deposition. High-temperature tube-blocking equipment was used to study scale deposition in a laboratory. The test enables deposition to take place within a capillary coil (heat exchanger) at a desired temperature and be monitored based on pressure buildup. Figure 2 presents a schematic of the equipment. During the test, the brine’s scale deposition rate—measured via an increase in delta pressure—in a 1-m-long capillary coil was measured at temperatures ranging from 80°C to 120°C. The synthetic brine consisted of separate cation and anion solutions, which were separately brought to the desired temperature in preheated coils and mixed together at the tee prior to entering the capillary coil. Pressure inside the capillary coil was monitored and logged on a PC. Increased pressure over time indicates that deposition is occurring within the capillary coil.

To mimic the brine chemistry in a thermal desalination plant, brine concentration factors of 1.5 and 2 were used in the high-temperature deposition test. Table 2 shows these water chemistries.

The test was conducted without antiscalant at temperatures of 80°C to 120°C in brine with a concentration factor of 1.5. Figure 3 shows the results. As expected, the increase in temperature increases the rate of blocking of the capillary coil with scale. To determine whether the rate of deposition is linear or nonlinear, the results were further analyzed by determining the time required to reach a delta pressure of 1 at different temperatures.

Table 3 illustrates the rate of scale deposition (delta pressure at 1x to reach delta pressure of 1) increases with temperature. These deposition rates are significantly different at various temperatures, suggesting that scale accumulating on the metal surface may be of a different composition. If it had been a single type of deposit with the same composition, a constant scale-deposition rate would have been obtained. It is worth noting that the rate of deposition in the same brine is 19 times faster at 130°C than at 80°C.

### Table 2. Synthetic brine chemistry for mixed scale deposition test

<table>
<thead>
<tr>
<th>Component</th>
<th>Brine concentration factor of 1.5 (mg/L)</th>
<th>Brine concentration factor of 2 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>600</td>
<td>800</td>
</tr>
<tr>
<td>Magnesium</td>
<td>1,803</td>
<td>2,404</td>
</tr>
<tr>
<td>Potassium</td>
<td>593</td>
<td>790</td>
</tr>
<tr>
<td>Sodium</td>
<td>13,690</td>
<td>18,254</td>
</tr>
<tr>
<td>Sulfate</td>
<td>3,935</td>
<td>5,246</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>278</td>
<td>374</td>
</tr>
<tr>
<td>Carbonate</td>
<td>139</td>
<td>184</td>
</tr>
<tr>
<td>Chloride</td>
<td>27,967</td>
<td>37,290</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>51,098</td>
<td>68,135</td>
</tr>
<tr>
<td>pH</td>
<td>8.5</td>
<td>8.64</td>
</tr>
</tbody>
</table>

### Table 3. Scale deposition rate at various temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time to reach delta pressure = 1 (min)</th>
<th>Rate of scale deposition based on delta pressure at 1x to reach delta pressure to 1 (psi/minutes)</th>
<th>Relative rate of deposition to 80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>38</td>
<td>0.0263</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>28</td>
<td>0.0357</td>
<td>1.36</td>
</tr>
<tr>
<td>110</td>
<td>10</td>
<td>0.1000</td>
<td>3.80</td>
</tr>
<tr>
<td>120</td>
<td>5</td>
<td>0.2000</td>
<td>7.60</td>
</tr>
<tr>
<td>130</td>
<td>2</td>
<td>0.5000</td>
<td>19.0</td>
</tr>
</tbody>
</table>
Antiscalant A was tested at a concentration factor of 1.5 at 110°C at 10 ppm and 12 ppm. Figure 4 shows the results.

The “pass” criteria used in this work was for the antiscalant dose level in the tube-blocking test to maintain a delta pressure less than 1 for 120 minutes. Using these criteria, the dose level of Antiscalant A required for a brine concentration of 1.5 at 110°C and 120°C (Figure 5) was 12 ppm and 20 ppm, respectively. The higher dose level at 120°C could have been caused by the increased temperature, as well as a change in composition of scale accumulating in the capillary coil.

A further test was carried out using a brine concentration factor of 2 at 110°C. Antiscalant A's dose level was tested from 40 ppm to 60 ppm, and Figure 6 shows the results.

Testing at a higher concentration factor of 2 at 110°C indicates that a 50-ppm dose of Antiscalant A is required to pass this test. Therefore, increasing the concentration factor at 110°C increases the Antiscalant A dose by 48 ppm for different brines. Again, this could result from differences in the composition of scale being controlled in brine concentration factors of 1.5 and 2 at the same temperature, 110°C. Saturation indices were investigated to better understand the chemistry of scales that would form under these conditions.

### Saturation Indices

The water chemistries shown in Table 3 were used to calculate the Stiff-and-Davis stability index (S&DSI) (Stiff and Davis, 1952), which is normally used for brines, and the individual saturation index using the solubility product $K_{i,p}$ of calcium carbonate (Equation 1), magnesium hydroxide (Equation 2), and calcium sulfate (Equation 3). The results are shown in Figures 7, 8, 9, and 10.

The analysis shows that the S&DSI increases with increasing temperatures and brine concentration (Figure 7). The deposition of calcium carbonate increases with increasing temperature and increasing brine concentration. However, S&DSI does not consider the precipitation of other salts, such as magnesium hydroxide and calcium sulfate. A different picture emerges if these salts are taken into consideration using the solubility product for the individual salts (Figures 8, 9 and 10).

Figures 8, 9, and 10 illustrate that the calcium carbonate deposition decreases with increasing temperature but increases with an increasing brine concentration factor of 1.5–2, because bicarbonate and carbonate alkalinity is being driven by temperature to form hydroxyl ions. These hydroxyl ions react with magnesium ions to form magnesium hydroxide.
Because of S&DSI limitations to predict calcium carbonate at high temperatures and brine concentrations, the author used the solubility product for individual salts to provide a realistic picture of salt precipitation from brines used in high-temperature tube-blocking equipment. Table 4 shows the saturation indices calculated for the brines. This analysis shows that the ratio of calcium carbonate to magnesium hydroxide and calcium sulfate differ with respect to temperature and the brine concentration factor. That is why a different dose level is required to control scale deposition in high-temperature tube-blocking equipment.

For all conditions in Table 4, the Antiscalant A dose required to control scaling was determined in the high-temperature tube-blocking test. Using information from scale deposition testing, the dose curve for Antiscalant A was developed for a magnesium saturation index, Figure 11, assuming the calcium carbonate saturation index is less than 30 and the calcium sulfate saturation index is less than 1.25.

When using this curve, the saturation indices should be calculated for the recycle brine or brine blowdown, because this varies based on operating conditions—e.g., seawater chemistry, top brine temperature, flow rates, and sponge-ball circulation. When the saturation indices are calculated for the brine and the dose level determined from the dosing curve (Figure 11), the dose level must be divided by the concentration factor to determine how much Antiscalant A is fed into the seawater. This dose level curve should be used as a guide for thermal desalination plants operating at top brine temperatures of 100–120°C. However, adjustments are necessary if heavy metal ions and silts are present in the seawater or brine.

In the past, antiscalant suppliers provided guidelines based on top brine temperature and antiscalant dose level for a plant operating with or without sponge-ball circulation. This type of curve can lead to an incorrect antiscalant dosing level being used. For example, if two plants are operating at the same top brine temperature but have different seawater feed chemistry or the brine concentration factor is different, the saturation indices of each plant’s brine would differ significantly. To accommodate this type of plant-to-plant variability, it is better to determine brine saturation indices and use a dosing curve similar to that shown in Figure 11.

**Monitoring Antiscalant**

Scaling often occurs because an antiscalant has been under dosed, usually resulting from dilution inaccuracies, dosing pump fluctuations, or dosing pipeline leaks. Therefore, there is significant benefit to measuring an antiscalant in the brine to confirm the amount present. To measure the amount of Antiscalant A polymer present in the brine, a new method based on fluorescence has been developed.

An inherent property of Antiscalant A is that it fluoresces and can be measured in a fluorimeter. A laboratory

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Brine concentration factor</th>
<th>Saturation Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calcium carbonate</td>
<td>Magnesium hydroxide</td>
</tr>
<tr>
<td>110</td>
<td>1.5</td>
<td>11.2</td>
</tr>
<tr>
<td>110</td>
<td>2</td>
<td>28.9</td>
</tr>
<tr>
<td>120</td>
<td>1.5</td>
<td>9.5</td>
</tr>
</tbody>
</table>
The data were used to generate a dose-level guide based on the saturation index of magnesium hydroxide for thermal desalination plants operating at temperatures of 100–120°C.

fluorimeter⁶ (Fluorimeter A) was used to determine the optimum emission and excitation wavelengths for the antiscalant in 1,000-ppm sodium chloride solution pH adjusted to 8 (Figure 12). The antiscalant was found to have an optimum excitation wavelength of 220 nm and optimum emission wavelength of 295 nm.

Another fluorimeter⁷ (Fluorimeter B) with excitation filters at 214 nm (+/- 5 nm) and emission filters at 300 nm (+/- 5 nm) was used to determine Antiscalant A’s calibration curves in brines with total dissolved solids (TDS) of 40,000 ppm and 70,000 ppm. Figure 13 shows the results.

Antiscalant A’s calibration curves are nonlinear in brines with a TDS range of 40,000–70,000 ppm. These calibrations were checked for reproducibility and found to be nearly identical. The accuracy of determining Antiscalant A’s concentration in these brines was confirmed by making up known amounts (1–5 ppm) and comparing them with the calibration curves shown in Figure 13. Within the laboratory, the accuracy was +/- 10 percent at 1 ppm and +/- 2 percent at 5 ppm and greater.

Conclusion
Antiscalant A, a biodegradable, phosphorus- and nitrogen-free polycarboxylic acid polymer, does not bioaccumulate in living organisms. Therefore, Antiscalant A is an environmentally friendly antiscalant that can be used in thermal desalination plants where environmental restriction or concerns exist.

Antiscalant A is an effective scale-control agent for calcium carbonate, magnesium hydroxide, and calcium sulfate on heat-transfer surfaces. The data were used to generate a dose-level guide based on the saturation index of magnesium hydroxide for thermal desalination plants operating at temperatures of 100–120°C. This would be a more realistic tool for predicting the dose level of Antiscalant A than the current method of using top brine temperatures vs. dose levels.

The intrinsic property of fluorescence in Antiscalant A was used to develop a method to monitor the antiscalant in seawater brines. Fluorimeter B can be used in the field to monitor Antiscalant A with an accuracy of less than +/- 10 percent at a 1-ppm dose level and +/- 2 percent at a 5-ppm dose level. Desalination plant operators can use this method to control Antiscalant A’s dose level in seawater brines and optimize the distiller dose if required.

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Footnotes
1WaterCycie, French Creek Software, Kimberton, Pa.
2Belgard EV and Belgard EV2000, Ciba-Geigy, Basel, Switzerland.
3Belgard EV2030 and Belgard EV2050, Ciba-Geigy, Basel, Switzerland.
4PMA-1, BWA Water Additives, Manchester, United Kingdom.
5BWA Water Additives, Manchester, United Kingdom.
6RF-1501, Shimatzu, Kyoto, Japan.
7Jenway Fluorimeter 6258, Jenway, Staffordshire, United Kingdom.

References

Editor’s Note
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