Examining Biodegradability of Water Treatment Additives

BY KELLY HARRIS

Across the globe environmental pollution is considered as a major concern for all industries. Many programs have been established for identifying and assessing substances which could cause long term harm. This “harm” includes substances which remain within the environment, building up in the tissue of the biological organisms that inhabits that area until such a level is reached that it manifests itself in a toxic way. These Persistent Organic Pollutants (POPs) or Persistent, Bio-accumulating, Toxic substances (PBTs) can be identified and characterized using a variety of tests. Once identified, classification depending on specific criteria can be achieved.

Unfortunately the hunt for “low harm” (i.e. biodegradable) inhibitors has meant that less effective products are sometimes selected due to their perceived “green” qualities. This is in spite of the fact that lower efficacy can actually result in increased chemical discharge back to the environment. In an ideal world a very small amount of chemical would be used which would then disappear completely. A survey of the currently available products shows that although this target has not been met, some products are definitely moving in the right direction.

Biodegradation

Biodegradation is a natural process by which organic substances are decomposed by microorganisms (mainly aerobic bacteria) into simpler substances such as carbon dioxide, water and ammonia. At the moment evidence of partial degradation is enough to meet most criteria and avoid categorization as a PBT or POP.

For measuring biodegradability, the most recognized tests are the Organization for Economic Cooperation and Development (OECD) series.

<p>| Table 1. Inherent biodegradability of commonly used scale inhibitors and the new ‘green’ inhibitors. |</p>
<table>
<thead>
<tr>
<th>INHIBITOR TYPE</th>
<th>ACRONYM</th>
<th>INHERENT BIODEGRADABILITY RESULT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphonates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBTC</td>
<td>17% in 28 days</td>
<td></td>
</tr>
<tr>
<td>ATMP</td>
<td>23% in 28 days</td>
<td></td>
</tr>
<tr>
<td>HEDP</td>
<td>33% in 28 days</td>
<td></td>
</tr>
<tr>
<td>Polyacrylates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAA</td>
<td>10% in 35 days</td>
<td></td>
</tr>
<tr>
<td>Phosphinopolyacrylates</td>
<td>PPCA</td>
<td>0% in 35 days</td>
</tr>
<tr>
<td>Polymalic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMA</td>
<td>18% in 35 days</td>
<td></td>
</tr>
<tr>
<td>Teropolymalic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAT</td>
<td>35% in 35 days</td>
<td></td>
</tr>
<tr>
<td>Sulfonic Acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPOCA</td>
<td>7% in 28 days (OECD 306)</td>
<td></td>
</tr>
<tr>
<td>Polyaspartic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PASP</td>
<td>83-87% in 28 days</td>
<td></td>
</tr>
<tr>
<td>Carboxy methyl imin</td>
<td>GMI</td>
<td>&gt;20% (OECD 306)</td>
</tr>
<tr>
<td>Polycarboxylic acid</td>
<td>PCA</td>
<td>68-6% in 28 days (OECD 306)</td>
</tr>
<tr>
<td>Maleic Acid Polymer</td>
<td>MAP</td>
<td>54-9% in 35 days</td>
</tr>
</tbody>
</table>

* OECD 302B test unless otherwise stated

Positive test means that ultimate biodegradation in the environment will occur. A failure does not mean that the chemical will not biodegrade at all, so instead inherent biodegradability tests may be performed.

Inherent tests

These tests have a high capacity for degradation with long exposure times and a high biomass to substance ratio, thus giving the substrate the best chance. Again, this is a laboratory test with a controlled and synthetic environment. A positive result will demonstrate the substrate is inherently biodegradable, but a negative result can still not rule out degradation in its final environment.

Simulation Tests

These tests use a low concentration of the chemical and are performed in an environment that closely mimics the real world. A positive result here strongly suggests that a chemical will biodegrade in the natural environment. A negative result will give an indication that the chemical is likely to be persistent.

By following this process of beginning with the ready biodegradability tests and moving down the chain, a good understanding of how a substance will behave in the environment can be obtained.
When this information is used in combination with the toxicity and bio-accumulation data, the impact of releasing a chemical into the environment can be assessed with a high degree of confidence. However, determining if a chemical biodegrades is only half the story, since all of this is futile if it does not do the job it was designed for.

**Scale inhibitors**

Scale inhibitors are chemical substances which when added at very low levels will reduce or prevent the formation of scale. There are a vast array available today including phosphate esters, phosphonates (PBTC, ATMP, HEDP), polyacrylates (PAA), phosphinopolyacrylates (PPCA), polymaleic acids (PMA), terpolymaleic acids (MAT), sul-
Figure 3. Percentage Calcium Carbonate Inhibition Versus Calcite Saturation Index On An ICW Rig

![Graph showing ICW Evaporative Rig Comparison of PBTC with PASP, PCA and MAP.]

fonic acid copolymers (SPOCA), polystyrene sulfonates, and more recently the so-called "green" inhibitors polyaspartic acid (PASP), carboxy methyl inulins (CMI), polycarboxylic acids (PCA) and maleic acid polymers (MAP).

The biodegradability of the current classes of inhibitors available in the market is shown in Table 1. HEDP and MAT, being above 30%, are only just considered as inherently biodegradable. Looking at the new generation of "green" inhibitors all four are well above what is required to be considered as non-persistent. However, the question remains - are the new class of "green" products effective scale inhibitors?

Scale formation

Scale is formed by the increasing concentration of scaling cations, such as calcium with scaling anions, such as carbonate. Once the concentration of ions exceeds super-saturation levels nucleation will occur, which leads to precipitation. What happens at the surface of this crystal depends upon the rates of formation and dissolution of the scale. Generally the rate of formation is greater thus leading to growth of the crystal, these crystals can then clump together to form larger crystals.

There are three mechanisms by which inhibitors can work to prevent the catastrophic build up of scale. At the nucleation stage (threshold inhibitors), at the growth stage (growth inhibitors) and finally the deposition stage (dispersants).

Calcium Carbonate Inhibitor Testing

In Industrial Water Treatment when testing for the efficiency of a scale inhibitor against calcium carbonate scale the following tests can be performed.

1. Calcium Carbonate jar test. This is a 30 minute homogeneous test which demonstrates the threshold inhibitor ability of a product.

2. Pilot Cooling Tower Evaporative Unit Test. This is designed to test both the threshold and dynamic inhibitor mechanisms against calcium carbonate under heat transfer conditions.

Calcium Carbonate Jar Test

Here air bubbling is used to facilitate carbon dioxide removal, which moves the equilibrium towards carbonate formation, thereby increasing the test severity by raising the pH of the test solution.

A solution containing calcium chloride (150mg/L calcium) and magnesium chloride (45 mg/L magnesium) is mixed with an equal volume of a solution containing sodium carbonate (51 mg/L carbonate) and sodium bicarbonate (269 mg/L bicarbonate) which already contains the additive to be tested. The air bubbled solution is heated at 70°C (158°F) for 30 minutes, after which time the solution is filtered and the calcium remaining in solution determined by EDTA titration. The higher the amount of calcium retained in solution the greater the scale inhibition ability of the product.

The results expressed as percentage inhibition against dose level are given in Figure 1. At 1 and 2 mg/L dose level HEDP and ATMP are clearly the most effective with PCA and MAP being the best amongst the "green" scale inhibitors. Once a 4 mg/L dose level has been reached a number of inhibitors are capable of 100% inhibition of calcium carbonate including PCA and MAP but PASP only reaches an 80% level. This may seem quite a high figure but unless 100% is reached calcium carbonate will form and ultimately greatly reduce the efficiency of the plant.

Pilot Cooling Tower Evaporative Unit Test

This dynamic test is designed to provide a realistic measure of an additive's

Figure 4. Calcium Carbonate Dynamic Scale Loop Test Results

![Graph showing the effects of different inhibitors on Calcium Carbonate formation over time.]

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ability to control calcium carbonate deposition. The Pilot Cooling Tower Evaporative unit (Figure 2) has constant make-up but has no blowdown, so the system water concentration increases with time as evaporation occurs. The system water is circulated over a 316 stainless steel heat exchanger. (surface temperature of approximately 70°C (158°F)). The evaporative region maintains bulk water temperature at 40°C (104°F), by passing air counter current to the water flow in the cooling tower. The higher the calcite saturation index (SI) that can be reached, the more efficient the inhibitor. Initial dose level of additives is 10 mg/L as solids.

In Figure 3, PBTC shows what level a good calcium carbonate inhibitor can achieve in this test. Its failure point occurs at a calcite SI of approximately 200.

Of the “green” inhibitors, MAP exhibited the best calcium carbonate control, reaching a calcite SI of 285. PCA also fared well with a failure point at 240 calcite SI. Both of these results are a significant increase over that reached by PBTC. PASP however gave a rather poor result failing at a calcite SI of approximately 80. This is less than one third of the level reached by MAP and PCA.

**Oil Industry**

When considering application in oilfields, performing dynamic scale loop tests is required to provide a good indication of inhibitor performance in the reservoir.

**Calcium Carbonate Dynamic Scale Loop Test**

In some ways the dynamic scale loop test is less severe than the threshold static jar test. The inhibitor is replenished therefore keeping it at a constant concentration. In the jar test when a crystal is formed some of the inhibitor is consumed as it binds onto the crystal surface. As inhibitor levels are not replenished, concentration will therefore drop over time. Having a constant inhibitor level throughout the dynamic test ensures that it is the growth inhibition mechanism that is being studied with metal surfaces acting as growth sites.

This test is conducted using synthetic Brent water. Separate solutions containing the anions and the cations are pumped through pre-heat coils at 90°C (194°F) and mixed in a T-piece prior to the 0.1 mm ID 1 m long 316 stainless steel test coil. During the test calcium carbonate deposition reduces the bore of the test coil causing an increase in pumping pressure. The rate of change in pressure across the coil is monitored with a pressure transducer and data captured for graphical representation later. The test is considered successful if the change in pressure remains below 1 psi (6.895 kPa) over a two hour period.

MAT, a commonly used inhibitor, demonstrates that a 2.5 mg/L dose level is sufficient to completely inhibit calcium carbonate scale formation (Figure 4). The “green” inhibitors PCA and MAP also display excellent scale inhibition at 2.5 mg/L.

PASP is unable to prevent scale formation at this dose, reaching 1 psi (6.895 kPa) in only 50 minutes.

**Conclusion**

All of these tests demonstrate that PCA and MAP offer a significant improvement over other biodegradable products such as PASP, and are also more efficient than their non-biodegradable counterparts, against calcium carbonate scale. A high result in a biodegradation test is a worthy aim however it should not be at the sacrifice of overall performance. A poor inhibitor could potentially do more damage in the long run as larger volumes of additive are required to control the scale and, therefore, much larger volumes are discharged into the environment. The focus of the water treatment industry has therefore never changed – to produce efficient products which prevent the formation of scale – now there is just an added caveat that they must do as little harm to the environment as possible. This study shows that although the problem has not been completely solved, we are certainly moving in the right direction. 

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About the author: Kelly Harris has a PhD in Synthetic Organic Chemistry at The University of Bath. Since joining BWA Water Additives in 2006, she has developed a number of scale inhibitors for oilfield and industrial water applications. She also has contributed to the development of oilfield and industrial water applications research.

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