Biodegradability of water treatment additives

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Across the globe, environmental pollution is a major concern for all industries. Many programmes 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 inhabit that area until they manifest themelves in a toxic way.

These persistent organic pollutants (POPs) or persistent, bio-accumulative and toxic substances (PBTs) can be identified and characterised using a variety of tests. Once identified, classification can be achieved depending on specific criteria.

For example, the OSPAR Convention aims to prevent further pollution by continuously reducing discharges, emissions and losses of hazardous substances, as identified by PBT criteria. The ultimate aim is to achieve concentrations in the marine environment of near background values for naturally occurring substances, or close to zero for man-made substances. Meanwhile the US EPA defines two sets of criteria for PBTs. Fitting into one means that emissions must be controlled, while in the other, they must eventually be banned.

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. Sometimes the decreased efficacy of these perceived green products may 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 micro-organisms, mainly aerobic bacteria, into simpler substances, such as CO_2, water and ammonia. At the moment, evidence of partial degradation is enough to meet most criteria and avoid categorisation as a PBT or POP. For measuring biodegradability, the most recognised tests are the OECD series:
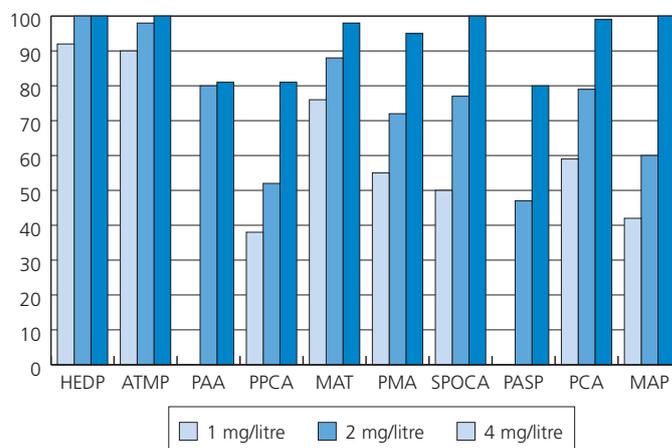

Figure 1 - $CaCO_3$ threshold test - percentage inhibition at specified dose level

- **Ready/ultimate biodegradability tests**, rigid laboratory screening tests with a high level of test substance (2-100 mg/litre). A positive test means that ultimate biodegradation in the environment will occur but a failure does not mean that the chemical will not biodegrade at all; it simply means that inherent biodegradability tests should be performed to determine the biodegrability profile
- **Inherent biodegradability tests**, another laboratory test in a controlled and synthetic environment, with a high capacity for degradation with long exposure times and a high biomass-to-substance ratio, thus giving substrates the best chance. A positive result will demonstrate that the substrate is inherently biodegradable, but a negative result may still not rule out degradation in its final environment
- **Simulation tests**, which use a low concentration of the chemical and are performed in an environment that closely mimics the real world. A positive result strongly suggests that a chemical will biodegrade in the natural environment, but a negative result indicates 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 this 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 originally designed for.

Scale of the problem

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 and HEDP), polyacrylates (PAAs), phosphinopolyacrylates (PPCAs), polymaleic acids (PMAs), terpolymaleic acids (MATs), sulfonic acid copolymers (SPOCAs), polyvinyl sulfonates and more recently the so called 'green' inhibitors, polyaspartic acid (PASP), carboxy methyl inulins (CMIs), polycarboxylic acids (PCAs) and maleic acid polymers (MAPs).

Table 1 - Inherent biodegradability of scale inhibitors

Inhibitor type	Acronym	Inherent biodegradability result*
Phosphonates	PBTC	17% in 28 days
	ATMP	23% in 28 days
	HEDP	33% in 28 days
Polyacrylates	PAA	10% in 35 days
Phosphinopolyacrylates	PPCA	0% in 35 days
Polymaleic	PMA	18% in 35 days
Terpolymaleic	MAT	35% in 35 days
Sulphonic acid co-polymers	SPOCA	7% in 28 days (OECD 306)
Polyaspartate	PASP	83-87% in 28 days
Carboxy methyl inulin	CMI	>20% (OECD 306)
Polycarboxylic acid	PCA	68.6% in 28 days (OECD 306)
Maleic acid polymer	MAP	54.9% in 35 days
* OECD 302B test unless otherwise stated		

Table 1 shows the biodegradability of the current classes of available inhibitors. HEDP and MAT, at above 30%, are only just considered as inherently biodegradable. All four of the new 'green' inhibitors are well above what is required to be considered as non-persistent. However, the question remains, are these effective scale inhibitors?

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 the growth of crystals, which 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: the nucleation stage (using threshhold inhibitors), the growth stage (growth inhibitors) and the deposition stage (dispersants).

Industrial water

In industrial water treatment, when testing for the efficiency of a scale inhibitor against calcium carbonate ($CaCO_3$) scale, two different tests can be performed.

The **$CaCO_3$ jar test** is a 30 minute homogeneous test which demonstrates the threshold inhibitor ability of a product. Air bubbling is used to facilitate CO_2 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 (150 mg/litre calcuim) and magnesium chloride (45 mg/litre magnesium) is mixed with an equal volume of a solution containing sodium carbonate (51 mg/litre carbonate) and sodium bicarbonate (269 mg/litre bicarbonate), which already contains the additive to be tested. The solution is heated at 70°C for 30 minutes, after which it is filtered and the calcium remaining is determined by EDTA titration.The more calcium retained in solution, the greater the scale inhibition ability of the product.

The results expressed as percentage inhibiton against dose level are shown in Figure 1. At 1 and 2 mg/litre 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/litre dose level has been reached, a number of inhibitors are capable of 100% inhibition of $CaCO_3$, including PCA and MAP, but PASP only reaches an 80% level. This may seem like quite a high figure but, unless 100% is reached, $CaCO_3$ will form and ultimately greatly reduce the efficiency of the plant.

The **pilot cooling tower evaporative unit test** is a dynamic test designed to provide a realistic measure of an additive's ability to control $CaCO_3$ deposition. In this test, the unit has constant make-up but 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 with a surface temperature of approximately 70°C. The evaporative region maintains bulk water temperature at 40°C by passing air counter current to the water flow in the cooling tower. The higher the calcite saturation index (SI) reached, the more efficient the inhibitor. The initial dose level of additives is 10 mg/litre as solids.
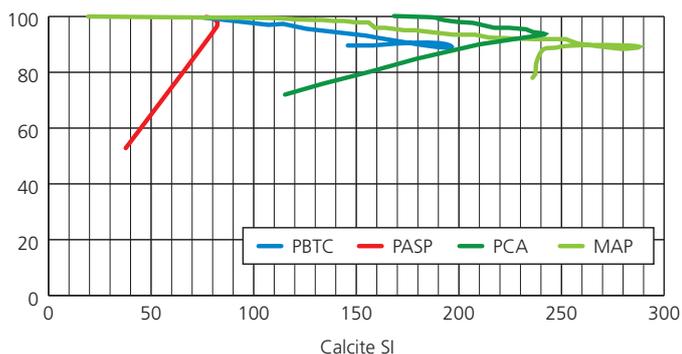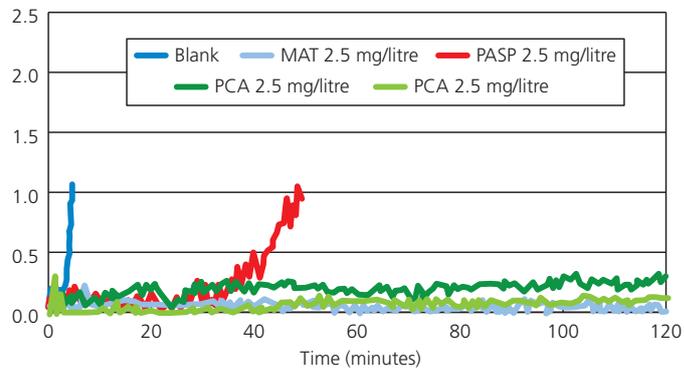

Figure 3 - $CaCO_3$ dynamic scale lop test results

Figure 2 shows what level a good $CaCO_3$ inhibitor can achieve in this test. PBTC's failure point occurs at a calcite SI of approximately 200. Of the 'green' inhibitors, MAP exhibited the best $CaCO_3$ control, reaching a calcite SI of 285. PCA also fared well, with a failure point at 240 calcite SI. Both were much better than PBTC, but PASP failed at a calcite SI of approximately 80.

Oilfield applications

When considering application in oilfields, it is important to provide a good indication of inhibitor performance in actual field condition. This is best done via a **$CaCO_3$ dynamic scale loop test**.

In some ways, this test is less severe than the threshold static jar test, as the inhibitor is replenished, 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, the 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.

Figure 3 shows results from conducting the $CaCO_3$ dynamic scale loop test using synthetic Brent water. Separate solutions containing the anions and the cations are pumped through pre-heat coils at 90°C and mixed in a T-piece prior to the 0.1 mm ID, 1 metre long 316 stainless steel test coil.

During the test, $CaCO_3$ 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 6.895 kPa for two hours.

Figure 3 shows that a 2.5 mg/litre dose level of MAT, a commonly used inhibitor, is sufficient to inhibit $CaCO_3$ scale formation completely. The 'green' inhibitors PCA and MAP also display excellent scale inhibition at 2.5 mg/litre. However, PASP, commonly perceived to be a 'green' inhibitor, is unable to prevent scale formation at this dose, reaching 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 $CaCO_3$ scale. A high result in a biodegradation test is a worthy aim, but should not be used if it means sacrificing 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 never changed. It seeks to produce efficient products that prevent the formation of scale, but now with the 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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Figure 2 - Percentage $CaCO_3$ inhibition versus calcite saturation index on an ICW rig