

OILFIELD TECHNOLOGY



THE MANY SHADES OF GREEN

Kelly Harris, BWA Water Additives, UK, takes a look at screening tests in order to find more environmentally friendly chemicals.

Since the 1972 Stockholm United Nations Conference on the Human Environment, environmental pollution has been considered as a major concern for all industries. Across the globe, a number of governments and regional economic integration organisations have since established programmes for identifying and assessing substances that could cause long term harm. This 'harm' is defined as substances that are resistant to degradation and accumulate in living organisms where they produce undesirable effects above a certain level of concentration. These Persistent Organic Pollutants (POPs) or Persistent, Bio-accumulating, Toxic substances (PBTs) are classified using a variety of tests and are subject to regulations concerning their use. These tests are dependent on the final destination of the chemical, and knowledge of how the environment will be impacted by its presence is paramount. Once identified, classification depending on specific criteria can be achieved. For example:

- The OSPAR (Oslo and Paris) Convention for the Protection of the Marine Environment of the North-East Atlantic, aims to prevent further pollution by continuously reducing discharges, emissions and losses of hazardous substances (identified by PBT criteria), with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances, or close to zero for man-made substances.
- The Environmental Protection Agency (EPA) in the USA defines two sets of criteria for PBTs. Fitting into one of which means emission must be controlled, and the other, for it to eventually be banned.

- ➔ The Canadian Government has a screening process that places substances that are persistent or bio-accumulating and inherently toxic into three categories depending on the outcome of further screening.

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 this lower efficacy may actually result in increased chemical discharge back to the environment. In an ideal world a very small amount of chemical would be used

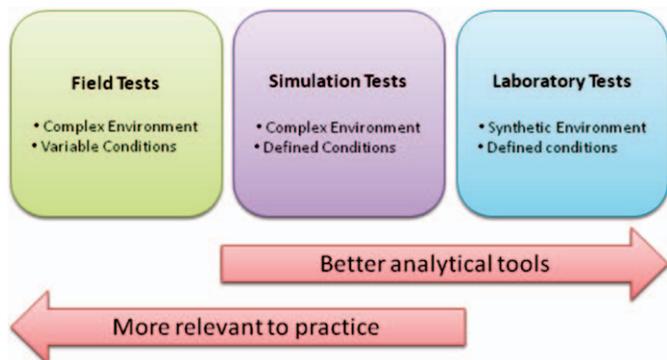


Figure 1. Schematic demonstration of the differences between laboratory tests and field tests.

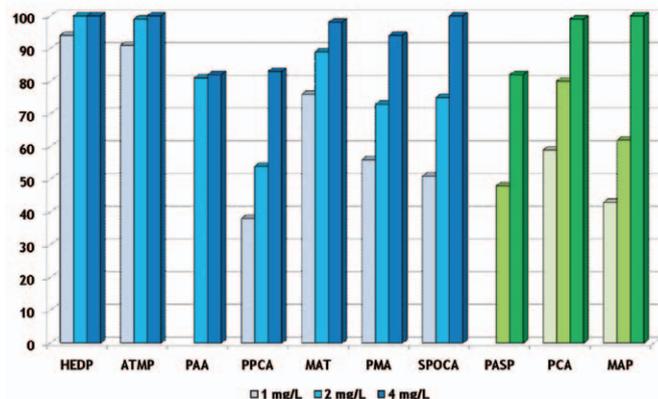


Figure 2. Calcium Carbonate Threshold Test - percentage inhibition at specified dose level.

Table 1. Inherent biodegradability of commonly used scale inhibitors and the new 'green' 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.

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 CO₂, 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 Organisation for Economic Co-operation and Development (OECD) series and include purely laboratory-based tests, as well as simulation and field-based tests.

The closer a test mimics the environment the less control there is in place and therefore the less reliable the data is.

In the laboratory tests, every chance is given for degradation to occur utilising high levels of test substance or, a low ratio of test substance to biomass with a long adaptation period, and a simplified environment. Simulation tests are a good central point with external factors, such as temperature and pH, controlled but a more realistic environment.

Within OECD guidelines a series of tests can be undertaken as follows:

Ready/ultimate tests

These are rigid screening tests with a high level of test substance (2 to 100 mg/L). They are laboratory tests, however, a 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 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 designed for.

Scale inhibitors

Water systems are ubiquitous with the chemical process industries (CPIs). The mixing, heating, concentrating or evaporating of water in these systems will form scale if they are left untreated.

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), sulfonic acid copolymers (SPOCA), polyvinyl 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. Before the push for 'green' products very few were actually biodegradable. HEDP and MAT, being above 30%, are only just considered as inherently biodegradable. Looking at the new generation of 'green' inhibitors it is clear to see the difference with all four 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 and barium with scaling anions, such as carbonate and sulphate. 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 that will eventually block the system. There are three mechanisms by which inhibitors can work to prevent the catastrophic build up of scale; at the nucleation stage, at the growth stage and finally the deposition stage.

Threshold inhibitor

The inhibitor binds with the scale forming ions, but unlike chelants the bound ions must be available to interact with their counter ions. This disrupts the ion cluster at the early equilibrium stages of crystal formation, thus disrupting them before they reach critical size for nucleation. As a result the ions dissociate releasing the inhibitor to repeat the process.

Growth inhibitor

This slows the growth of the scale by blocking the active edges of the crystal. Once the inhibitor has bound to the lattice, the crystal will form much more slowly and be distorted. Often they are much more rounded in shape which makes them less likely to adhere to surfaces and more easily dispersed throughout the system.

Dispersant

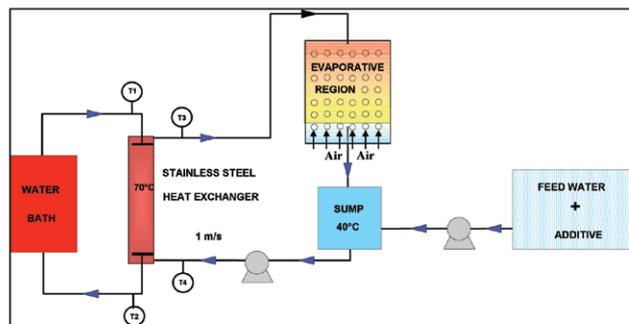


Figure 3. Schematic diagram of PCT with conditions of operation.

Table 2. Calcium Carbonate Dynamic Scale Loop Test water chemistry

Ion	Concentration mg/L
Calcium	350
Magnesium	56
Sodium	10 077
Potassium	283
Barium	50
Strontium	50
Bicarbonate	1000
Chloride	16 058
Sulphate	0
TDS	27 924

Table 3. Barium sulphate test water

Ion	Concentration mg/L
Calcium	636
Magnesium	634
Sodium	14 760
Potassium	446
Barium	120
Strontium	190
Bicarbonate	0
Chloride	26 930
Sulphate	530
TDS	44 246
pH	5.5

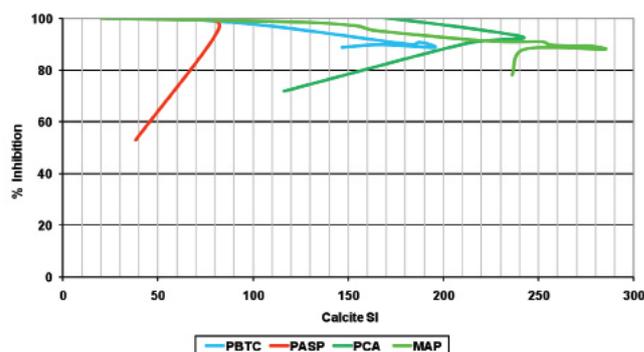


Figure 4. Percentage calcium carbonate inhibition versus Calcite Saturation Index on an ICW rig.

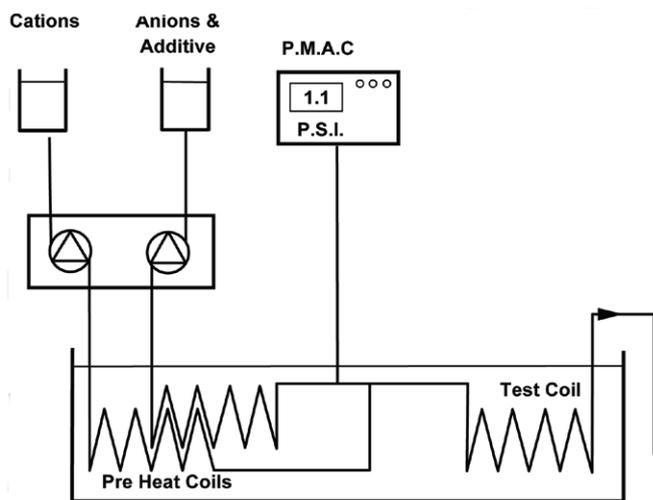


Figure 5. Dynamic Scale Loop Test Schematic.

Prevents the crystals coming together and forming a large body of scale. The inhibitor will interact with the surface and repulse other charged particles so that they do not bind.

Industrial Water Treatment (IWT)

In the IWT area the most commonly encountered type of scale is calcium carbonate, which may occur in three possible crystal forms – aragonite, calcite and vaterite. When testing for the efficiency of a scale inhibitor against calcium carbonate scale the following tests can be performed:

Calcium Carbonate Jar Test

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

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 CO₂ 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 and magnesium chloride is mixed with an equal volume of a solution containing sodium carbonate and sodium 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 2. 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 like 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 ability to control calcium carbonate deposition. The Pilot Cooling Tower Evaporative unit 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. The heat exchanger is heated by passing hot water through the tube. The surface temperature of the heat exchanger is 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. A schematic diagram of the equipment used is given in Figure 3. Initial dose level of additives is 10 mg/L as solids.

In Figure 4, 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 both the calcium carbonate and the barium sulphate 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, the water chemistry for which is given in Table 2. 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. A schematic representation of this apparatus is shown in Figure 5. 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 6). 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.

Barium Sulphate Dynamic Scale Loop Test

The water chemistry for this dynamic scale loop test is given in Table 3 and is equivalent to a 80:20 Troll:Seawater mixture. The anion and cation solutions, this time with no inhibitor present, are pumped through preheat 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. Barium sulphate deposition reduces the bore of the test coil causing an increase in pumping pressure. Once a 1 psi (6.895 kPa) change in pressure has been achieved, a third solution containing anions plus inhibitor replaces the anions solution. The test is run for 2 hours unless the additive fails to prevent further barium sulphate scale.

Figure 7 illustrates the data for MAT and the three 'green' inhibitors PASP, PCA and MAP. At a 4 mg/L dose level MAT was able to stop deposition completely thus leading to no further increase in pressure. PASP, PCA and MAP were equally efficient at this dose level. This demonstrates that in this test the 'green' inhibitors are as efficient as those already in common use.

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 that

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. **OT**

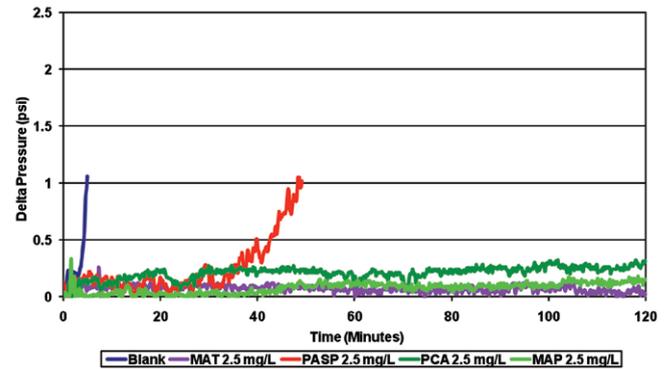


Figure 6. Calcium Carbonate Dynamic Scale Loop Test Results.

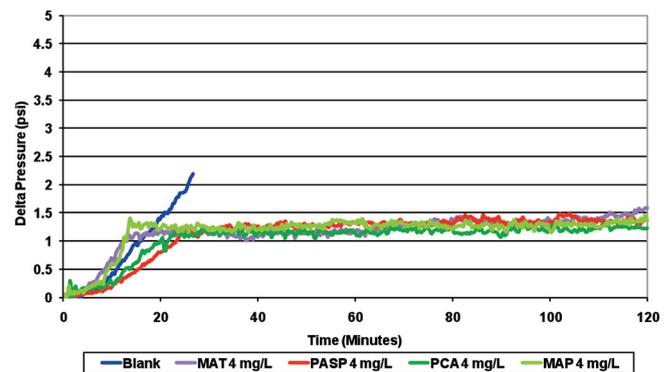


Figure 7. Barium Sulphate Dynamic Scale Loop Test.