Theoretical and practical experience of calcium phosphate inhibition in RO waters.

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ABSTRACT
The increasing trend over the last ten years to use waste water as a feed source for reverse osmosis membrane plant has resulted in an increase in calcium phosphate scaling on membrane surfaces. This is due to much higher levels of phosphate in waste water typically 10-30 mg/l as compared with a groundwater source which may have only 1-5 mg/l of phosphate. These higher phosphate levels resulting from effluent breakdown in primary sewage treatment causes calcium phosphate solubility to be exceeded in reverse osmosis membrane systems resulting in scale formation. Conventional antiscalant chemistry based on threshold inhibition and crystal distortion has had poor results in high phosphate high pH waters. Dosing large quantities of acid to lower the scaling tendency is no longer an acceptable approach. This paper investigates the complexities of multiple species of calcium phosphate with varying solubility’s all contributing to an amorphous deposit. Research conducted by the medical community into calcium phosphate based cement for bone and teeth repair has been applied to theories of calcium phosphate precipitation and crystal growth. Highly active calcium phosphate threshold inhibitors were tested in the laboratory and a development product Genesys PHO (Antiscalant B) formulated which was then used in three waste water pilot plants and compared with conventional antiscalants. The results of this beta testing showed the new formulation out performed the conventional antiscalants and that calcium phosphate scaling could be controlled without the need for pH correction through acid dosing in once through RO plants. The third RO pilot plant was a recycled system where scale formation was not prevented. The results from another two high pH, high phosphate agricultural leachate waters are also presented.

Understanding the mechanisms of calcium phosphate deposition and the lack of crystal growth has enabled a highly active threshold inhibitor antiscalant to be formulated which is effective at preventing calcium phosphate scale formation in high phosphate, high pH feed waters to RO membranes without the need for acid dosing.
I. INTRODUCTION

Over the past ten years there has been a dramatic increase in the number of reverse osmosis and nano-filtration plant that operate using effluent water as a feed water source. Many of these plants have suffered from phosphate scaling in the second stage of the membranes. Conventional chemical antiscalant treatment has shown to be ineffective at preventing scale formation which results in poor plant performance. This paper presents the results of a new antiscalant developed in the laboratory and then beta tested in the field. Three trial site results are presented here.

1.1 HIGH PHOSPHATE FEED WATERS

In discussing the presence of phosphate in feed water it is important to understand where phosphate originates and how man’s intervention has increased the amount of soluble phosphate in our water supplies. The phosphorus cycle is a “sedimentary” cycle in which the earth’s crust is the major reservoir. On land, phosphate rock deposits are the primary source of phosphorus. Through natural and human induced erosion processes, phosphates from these rock deposits are washed into rivers, and eventually to the oceans, where they form shallow and deep ocean phosphate rock deposits. Animal bones and teeth are made up of calcium phosphate and contribute to the cycle. Phosphate levels have risen due to:

1.1.1 Detergent Contamination – phosphate is used in detergents as a builder to counteract the effects of Calcium and Magnesium hardness in the water which reduces the surfactant and cleaning effect of detergents. The phosphate does not degrade in the effluent water and therefore persists after effluent treatment. Excess phosphate in groundwater and waterways causes an ecological imbalance which can result in algal blooms and the creation of anaerobic conditions which affects the natural aquatic life. Due to this the use of phosphate based detergents were banned in most US states in the 1980’s and manufacturers reformulated products with bio-degradable surfactants and builders.

1.1.2 Sewage and effluent recovery – in some areas of water scarcity around the world there is an increase in the re-use of treated effluent water for agricultural purposes and recharging of surface water and aquifers. Because phosphate removal is difficult and costly this practice has a tendency to increase the levels of phosphate in ground and surface waters. With increasing re-use of water this trend is likely to increase around the world.

1.1.3 Fertiliser contamination – phosphate is an important compound for plant growth. The use of phosphate fertiliser in the US increased four times from 1945 - 1985 and has been constant since, with 2 million tons of phosphorous being applied as fertiliser and another 2 million tons of phosphorous via manure. Phosphate is not very mobile and tends to remain attached to solid particles rather than dissolve. This means that during flooding and soil erosion a large amount of phosphate can be washed into waterways [2].

1.1.4 Geology – Over 70% of the world’s phosphate is mined in US, China, Morocco, West Sahara and Russia. Erosion and dissolution of phosphate bearing sedimentary rocks will create local high spots of soluble phosphate in groundwater.
II. WASTEWATER RO PLANT

As the world’s sources of fresh water diminish the high energy costs and environmental profile associated with desalinating sea water is making recycling water an increasingly attractive option. This includes taking municipal waste water and purifying it through UF/NF/RO plant and utilising agricultural and mining run-off water and leachate.

Over the last ten years there has been a huge increase in the number of wastewater RO plant. According to IDA 19th Inventory there are 713 plants worldwide with a combined daily capacity of 2,342,079 m³/day. The top five countries using reverse osmosis wastewater plant are shown below in Figure 1.

<table>
<thead>
<tr>
<th>Country</th>
<th>Plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Japan</td>
<td>220</td>
</tr>
<tr>
<td>USA</td>
<td>201</td>
</tr>
<tr>
<td>Spain</td>
<td>35</td>
</tr>
<tr>
<td>Germany</td>
<td>30</td>
</tr>
<tr>
<td>Taiwan</td>
<td>24</td>
</tr>
</tbody>
</table>

Figure 1: Top Five countries with RO waste water treatment plant [1].

There are only seven out of 1,868 reverse osmosis plants in the Middle East that are fed with waste water. Included in this seven is Sulaibiya in Kuwait which produces 375,000 m³/day of treated water and is the biggest waste water re-use plant in the world. Water for agriculture, irrigation and aquifer recharge is available at various levels of treatment including secondary, tertiary, UF and RO to drinking water standards although it is not currently used for drinking. The general lack of plant in the Middle East may be due to religious and cultural views regarding the re-use and human consumption of recycled water which may include some human effluent. A recent on-line study of 1,000 respondents showed “the Australian population clearly discriminates between recycled and desalinated water”. Furthermore “respondents clearly understand that recycled water is the more environmentally friendly option, whereas desalinated water is perceived as less risky from a public health point of view [2].” The state government of Queensland has recently awarded a contract to recycle some 200,000 m³/day of wastewater from Oxley, Wacol, Goodoa, Luggage Point and Gibson Island and purify it using MF/UF/RO and UV.

Leachate and polluted run-off from the mining and agricultural industries is increasingly being treated using UF/NF/RO. This minimises the environmental impact of high nutrients or toxic heavy metals into the waterways. The concentrate water from agricultural leachate can be used for irrigation and fertilisation and product water as a supplemental pure water supply.

Waste water phosphate levels can be 20-30 mg/l and some agricultural leachates can be as much as 100 mg/l. The combination of raised phosphate levels with high calcium and bicarbonate level means there is a high likelihood of phosphate scale formation on the membranes.
III. PHOSPHATE CHEMISTRY

Phosphate is a salt of phosphoric acid. The phosphate ion is polyatomic consisting of one central phosphorous atom surrounded by four identical oxygen atoms in a tetrahedral arrangement. The phosphate ion carries a negative three charge and can exist in the following forms in solution as pH becomes increasingly acidic:

- Phosphate ion \( -\ PO_4^{3-} \)
- Hydrogenphosphate ion \( -\ HPO_4^{2-} \)
- Dihydrogenphosphate ion \( -\ H_2PO_4^- \)
- Phosphoric acid \( -\ H_3PO_4 \)

It is a hypervalent molecule as the phosphorous atom has 10 electrons in its valence shell. There are many types of phosphate salts because phosphate can form many polymeric ions. The most common forms are summarised in the Table 1 below:

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Formula</th>
<th>Abb. Name</th>
<th>Mineral Name</th>
<th>Structure</th>
<th>Solubility Product mol/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous calcium phosphate rock</td>
<td>( Ca_9(PO_4)_6 )</td>
<td>ACP</td>
<td>Amorphous</td>
<td>Amorphous</td>
<td></td>
</tr>
<tr>
<td>Monocalcium phosphate</td>
<td>( Ca(H_2PO_4)_2 )</td>
<td>MCP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dicalcium phosphate dihydrate</td>
<td>( CaHPO_4\cdot2H_2O )</td>
<td>DCPD</td>
<td>Brushite</td>
<td>Amorphous</td>
<td>( 2.32 \times 10^{-7} )</td>
</tr>
<tr>
<td>Dicalcium phosphate</td>
<td>( CaHPO_4 )</td>
<td>DCP</td>
<td>Monetite</td>
<td>Amorphous</td>
<td>( 1 \times 10^{-7} )</td>
</tr>
<tr>
<td>Tricalcium phosphate</td>
<td>( Ca_3(PO_4)_2 )</td>
<td>TCP</td>
<td>Whitlockite</td>
<td>Amorphous</td>
<td>( 2.07 \times 10^{-33} )</td>
</tr>
<tr>
<td>Tetracalcium phosphate</td>
<td>( Ca_4O(PO_4)_2 )</td>
<td>TTCP</td>
<td>Hilgenstockite</td>
<td>Amorphous</td>
<td></td>
</tr>
<tr>
<td>Pentacalcium hydroxyapatite</td>
<td>( Ca_5(PO_4)_3(OH) )</td>
<td>HAP</td>
<td>Hydroxyapatite</td>
<td>Hexagonal</td>
<td>( 2.34 \times 10^{-59} )</td>
</tr>
<tr>
<td>Pentacalcium fluoroapatite</td>
<td>( Ca_5(PO_4)_3(F) )</td>
<td>FAP</td>
<td>Fluoroapatite</td>
<td>Hexagonal</td>
<td>( 3.16 \times 10^{-60} )</td>
</tr>
<tr>
<td>Octacalcium phosphate</td>
<td>( Ca_8(HPO_4)_2(PO_4)_4 )</td>
<td>OCP</td>
<td></td>
<td></td>
<td>( 2 \times 10^{-49} )</td>
</tr>
<tr>
<td>Calcium pyrophosphate</td>
<td>( Ca_2P_2O_7 )</td>
<td>CPP</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Various forms of Calcium orthophosphate

The thermodynamically most stable form is calcium hydroxyapatite (HAP) and calcium fluoroapatite, but they do not form readily even when supersaturated. Other mineral phases such as dicalcium phosphate dihydrate (DCPD) octacalcium phosphate (OCP) and amorphous tricalcium phosphate (TCP) form as precursors that transform to HAP [3]. HAP is generally present at pH above 4.2 and below that DCPD is the stable form. The solubility of calcium phosphate minerals generally increases with temperature however with HAP and OCP the solubility trend reverses at higher temperatures above 20°C. The temperature dependence of amorphous TCP is not consistent. The formation of calcium
phosphate deposits is further confused by the potential for supersaturating of solutions to occur without precipitation due to the lack of epitaxial growth surfaces [4]. Ordered crystalline growth may be delayed past the theoretical saturation point where localised surface symmetry is not conducive to enhancing the nucleation and concentrating affect of ions in solution.

It would appear that localised factors of pH temperature and surface dynamics within a reverse osmosis membrane can result in simultaneous formation of salts with different stoichiometries which can then interchange between the varieties described in Table 1. Feenstra and de Bruyn found that in neutral and slightly alkaline pH conditions that an amorphous calcium phosphate phase precipitated and served as a template for the heterogenous nucleation of OCP which in turn lead to the epitaxial growth of HAP [5]. In conditions when pH>9 amorphous calcium phosphates (ACP’s) are thought to convert directly into HAP whereas at pH 7-9 they are converted to a precursor OCP phase and then to HAP Thus in a typical reverse osmosis membrane plant with high phosphate feed water there is a high likelihood of a heterogenous precipitate of ACP and octacalcium phosphate OCP. Recent studies on the growth of dentine by Dahl, Veiss and George have demonstrated the growth of hydroxyapatite crystals from an amorphous calcium phosphate precipitate but only after a period of one week in a stagnant supersaturated solution as shown in Figure 2 [6].

Sequential appearance of deposited particles accompanying the hydroxyapatite nucleation and growth process.

a, During the first several hours after the start of nucleation, only amorphous calcium phosphate was observed.

b,c, From day one to day three, a series of intermediate structures were observed.

d, After one week of incubation, only plate-shaped hydroxyapatite crystals were observed. Each scale bar = 2 µm.

Figure 2: Stages of HAP crystal formation in dentine.

Hydroxyapatite is rarely found when autopsies are carried out on membranes. The usual form of deposit in membranes is a none-crystalline state as shown in Figure 3a. The deposit does not tend to damage the membrane surface as there is no abrasion or cutting action as crystals do not tend to grow. On rare occasions a distinct crystal shape will be found which is definitely calcium phosphate and probably in the form of hydroxyapatite. See Figure 3b.
The reason for the rarity of HAP formation may be due in part to the dynamic environment of membrane whereby continuous movement of water does not allow time for crystal formation to occur. It may be that the crystal example shown above (Figure 3b) was formed during a period of shutdown for three days when membrane flushing was not carried and a concentrated solution had time to develop HAP crystals. The solubility products for the various calcium phosphate forms shown in Table 2 are very different and quoted at varying levels by different researchers. Indeed a recent study by Chen, Darwell and Leung using solid titration and laser scattering end-point detection showed that HAP solubility “now differs substantially from results of previous studies (i.e. much lower).” (See Figure 4) [7]. These results compare with a traditional view (Figure 5) that has the solubility product of HAP and other forms of calcium phosphate potentially a lot higher than reality. This may go some way to explain the membrane scaling issues that seem to be increasingly frequent with phosphate loaded feed waters.
IV. CALCIUM PHOSPHATE INHIBITION

Calcium orthophosphate deposition tends to occur in the last membrane of the last stage of the RO plant where the concentration of ions is at its highest. An insoluble very thin 50 – 200 µm amorphous non-crystalline mat appears at the membrane surface. This deposit can build up very rapidly resulting in a reduction of permeate flow rate of 20 – 40 % in 2 hours. Another indicator of deposition taking place is an increase in feed and differential pressure. The calcium o-phosphate deposit is relatively easy to remove using acid cleaners. On some occasions iron or aluminium complexes may make up a proportion of the deposit and an alkaline wash with surfactant and chelating properties will also assist deposit removal.

Inhibition of calcium phosphate in the RO plant can be achieved by reducing pH by acid dosing. However there are obvious disadvantages with acid dosing:

- Health and Safety and environmental implications of transporting, handling and storing acid.
- Large quantities of acid are required where there is a high bicarbonate level in the feed water.
- Acid dosing will increase the CO₂ concentration in the permeate making it more corrosive.
- Dosing acid to the feed system to lower the pH makes the plant more susceptible to corrosion and subsequently to Iron deposition in the membranes.

Calcium phosphate inhibition has been well understood and documented by the water treatment industry for more than half a century. Sodium phosphate salts have been used in low and high pressure boilers where it forms a calcium phosphate sludge in the bulk water phase rather than as calcium scales at the heating surfaces; the sludge is then ‘mobilised’ by an organic conditioner. In cooling water inorganic polyphosphates have been used at low levels for corrosion control because polyphosphate is a cathodic inhibitor, much favoured by the water treatment industry. The reversion of polyphosphate to orthophosphate and the subsequent formation of calcium phosphate scales at the heat transfer surfaces or in cooling tower packing led to the use of calcium phosphate dispersants. The inhibitors used in boiler and cooling water as ‘sludge conditioners’ were almost exclusively based on polymeric dispersants. When membrane systems were first exposed to phosphate bearing waters, inhibitors that had proven successful for years in steam generation and cooling water applications were found to be of little value in controlling calcium phosphate.

Traditionally the ways to avoid calcium o-phosphate crystals, as other scales, were:

- Mixture of polymers, mainly coming from acrylic and maleic acids, using the crystal distortion and dispersion properties of the polymers.
- Mixture of phosphonates, using the threshold effect properties of some phosphonates.

Figure 6: Crystal distortion mechanism.
Having researched the stages of deposit formation it is clear that at the operating temperatures and pH range of Reverse Osmosis plant the precipitated solids are amorphous and can adopt varying localised forms. Crystal growth as shown in Figure 6 is not a significant process in calcium phosphate deposit formation therefore attention was turned away from the use of crystal distortion and dispersion polymers. The product investigation concentrated on increasing the threshold inhibiting effect of a phosphonate inhibitor by a synergistic blend of organic chemicals. Threshold inhibition as shown in Figure 7 inhibits the ionic ordering and nucleation stage of precipitation thus allowing the calculated solubility of ionic solutions to be exceeded. Laboratory analysis was carried out on a number of advanced threshold inhibitors and the most effective product which was compatible with the existing phosphonate inhibitor was a polymeric compound.

![Figure 7: Threshold inhibition mechanism.](image)

**V. LABORATORY ANALYSIS**

The first stage of the laboratory analysis was to produce calcium phosphate saturation curves. Solutions were made up with 1,000 mg/l sodium, chloride between 1,500 and 2,500 mg/l dependant on calcium level and sulphate 200 mg/l. The solubility index (amount of calcium and phosphate ions that can be held in solution) was then determined using six versions of the standard solution with varying calcium and phosphate ion concentrations and at temperatures of 25 and 30°C and a pH of 8.0. From these tables (see Table 2) the efficacy of the various inhibitor formulations with dispersants and polymeric compounds was tested until the best performing products were isolated and blended into the development product Genesys PHO (antiscalant B) formulations. From the six tables of saturation and antiscalant B dose rate, the results were plotted and a theoretical dose rate curve established. (Figure 8)

<table>
<thead>
<tr>
<th>PO₄ as ion</th>
<th>% Calcium Phosphate Saturation @ 150mg/l Ca as ion 30°C</th>
<th>Antiscalant B dose rate mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>20</td>
<td>787</td>
<td>5</td>
</tr>
<tr>
<td>30</td>
<td>1744</td>
<td>8</td>
</tr>
<tr>
<td>40</td>
<td>3055</td>
<td>12</td>
</tr>
<tr>
<td>50</td>
<td>4704</td>
<td>16</td>
</tr>
<tr>
<td>60</td>
<td>6676</td>
<td>19</td>
</tr>
<tr>
<td>70</td>
<td>8955</td>
<td>23</td>
</tr>
<tr>
<td>80</td>
<td>11526</td>
<td>26</td>
</tr>
<tr>
<td>90</td>
<td>14377</td>
<td>29</td>
</tr>
<tr>
<td>100</td>
<td>17493</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 2: Saturation index of Calcium Phosphate

![Figure 8: Antiscalant B dosage curve](image)
VI. HIGH PHOSPHATE FIELD TRIALS

Having identified a trial product in the laboratory that exhibited phosphate scale inhibiting properties vastly superior to conventional scale inhibitors three sites were identified to carry out some beta testing. The first site allowed side by side comparisons with conventional inhibitors. The remaining two sites have had product in use over an extended period.

6.1. Field Trial 1 – Alicante

The trial plant consisted of three Reverse Osmosis trains being supplied with treated municipal wastewater with ultrafiltration membrane pre-treatment supplied by three different manufacturers. The feed water was heavily scale forming with calcium levels of ~110 mg/l, bicarbonate ~420 mg/l and 10-20 mg/l of phosphate. The feed pH was 7.2 -8.2 and recovery rates at a theoretical 65-70%. Based on the feedwater analysis in Table 3 the Genesys Membrane Master scaling prediction software indicated that the solubilities of calcium carbonate, calcium phosphate and iron would be exceeded. Iron and calcium carbonate scaling could easily be controlled using a conventional phosphonate threshold scale inhibitor. However to reduce calcium phosphate solubility to 90% while using the standard antiscalant the feed water pH would have to be reduced to pH 6.2 which meant dosing 66kg of 35% active hydrochloric acid per day.

<table>
<thead>
<tr>
<th>Cations</th>
<th>mg/l</th>
<th>Anions</th>
<th>mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>160</td>
<td>Sulphate</td>
<td>287</td>
</tr>
<tr>
<td>Magnesium</td>
<td>534</td>
<td>Chloride</td>
<td>443</td>
</tr>
<tr>
<td>Sodium</td>
<td>269</td>
<td>Bicarbonate</td>
<td>401</td>
</tr>
<tr>
<td>Iron</td>
<td>0.05</td>
<td>Nitrate</td>
<td>0.5</td>
</tr>
<tr>
<td>pH</td>
<td>7.35</td>
<td>Silica</td>
<td>12.44</td>
</tr>
<tr>
<td>TDS</td>
<td>1691</td>
<td>Phosphate</td>
<td>19</td>
</tr>
<tr>
<td>Feed Pressure</td>
<td>10 Bar</td>
<td>Product Flow</td>
<td>132m3/day</td>
</tr>
<tr>
<td>Recovery Rate</td>
<td>75%</td>
<td>Feed Flow</td>
<td>176 m3/day</td>
</tr>
</tbody>
</table>

Table 3 Pilot Plant 1 operating data.

The trial objective was to record the performance of a conventional antiscalant and calcium phosphate specific antiscalant B with and without the use of acid to lower the feed pH. The trials were to run on three trains with different UF nanofiltration membranes. Parameters of feed, product and concentrate flow and pressure were used as indicators of membrane scaling.

6.1.1 Pilot Plant 1 Results – feed, product and concentrate flow rates were monitored for six months. Antiscalant A was dosed at 2.7 mg/l as per the manufacturer’s recommendations without acid for a period of four and a half months. pH levels varied between 7 and 7.7. After one month there was a rapid decline in flow rates due to calcium phosphate scaling and a cycle of acid cleaning to recover performance began. Following a clean of all the membranes Antiscalant B was dosed at 3 mg/l initially with hydrochloric acid to control pH at 6.1. The acid dose was gradually reduced and stopped completely after 20 days whereupon the pH range continued to fluctuate as before from 7 to 7.7. The dosage rate of antiscalant B without acid was increased to 4 mg/l initially and gradually reduced to only 2.0 mg/l without any reduction in flow rates or increase in pressure. (see Figure 9 and 10).
Figure 9: Plant flow rate with antiscalant A and B.

Figure 10: Plant pressure with antiscalant A and B.
6.1.2 Pilot Plant 2 Results – this plant had a different NF membrane pre-treatment manufacturer but was otherwise identical to Plant 1. A different scale inhibitor antiscalant C was used initially on this plant dosed at 8 mg/l in conjunction with acid controlled pH adjustment to 7.0.

After a period of one month there was a dramatic and rapid reduction in flow rate. The membranes were acid cleaned and antiscalant dosage resumed with an increased acid dosage to reduce the pH to 6.8. After two months antiscalant A, which had been used on Pilot Plant 1 with poor results replaced antiscalant C. The dose rate was 2 mg/l and acid was dosed to maintain the pH at 6.8. After just 4 days there was a dramatic loss of flow and increased pressure indicating calcium phosphate deposition.

The membranes were acid cleaned and antiscalant B was dosed initially at 3 mg/l with pH control at 6.1 to provide some additional on-line cleaning. The acid dose was gradually reduced and removed after twenty days and the antiscalant B dosage increased initially to 4 mg/l. The dosage rate was gradually reduced to 2.0 mg/l without any decrease in flow rates or increase in pressures. (see Figure 11 and 12).

A significant fluctuation in flow rates and pressures was seen during a period of interruption to electricity supply. The membranes were not flushed during this period and some deposition occurred which resulted in an increase in pressure when the plant came back on line.

Figure 11: Pilot Plant 2 flow rates with antiscalant A, B, and C.
6.1.3 **Pilot Plant 3** - was of a recycle design and suffered from heavy membrane fouling requiring three cleans during the two-month trial. Around 15% of the concentrate water was injected back into the RO plant feed water. This increases the scaling potential of the water as a proportion of the normally soluble species in the water can have a very long half-life in the system resulting in precipitation and scale formation. This phenomenon is consistent with research conducted by Greenberg on calcium phosphate precipitation where a recycled pilot RO system was used [8].

6.1.4 **Conclusions of Field Trial 1** - Genesys PHO prevented calcium orthophosphate precipitation in the membranes without the need for acid dosing and with extremely high levels of phosphate in excess of over 75 mg/l in the concentrate. Precipitation occurred when there was inadequate flushing or recycled concentrate made the feed water untreatable.

6.2 **Feed trial 2 – Murcia**

This reverse osmosis plant in Murcia had an agricultural leachate as the feed. The pre-treatment consisted of sand filtration with flocculant dosed at 3 mg/L. The leachate not only contained a high level of phosphates (~100 mg/L PO₄), but also a high calcium loading of 280 mg/L, as well as ~75 mg/L of bicarbonate in the acid dosed feed. The pH varied form 7.2 – 8.2 and product water output was 200m³/day.

6.2.1 **Results** - The plant has been operated with antiscalant B since November 2005 at a dosage rate of 4.3 mg/l. Acid was dosed to control the feed pH at 6.6. There were no fouling problems. The second phase was to progressively reduce the acid dosage. This was successful up to a value of pH 7.25, but it was not possible to increase the pH further during this period due to a highly variable feed quality. Quite frequently the feed water pH and bicarbonate concentration was so high that without acid dosing the Langelier Saturation Index of the concentrate would have been higher than 3.1. For this reason during the second phase of this trial, the feed water pH never surpassed 7.5. The third phase will be to slowly
decrease the Antiscalant B dosage rate, once the higher operating pH is stable. Regular alkaline cleans have been carried out in order to remove biofilm and organic matter from the first stage.

6.2.2 Conclusions - At a dosage rate of 3.7 – 5.0 mg/l of antiscalant B to the feed, and operating at pH values not higher than 7.25, no problems associated with calcium ortho-phosphate deposition have been identified. Consequently antiscalant B has been successful at controlling high phosphate levels, although further information under higher pH and lower antiscalant dosage conditions will extend operating information.

6.3 Feed trial 3 – Granada.
The third plant was situated in Granada and consisted of a 1,200 m³/day RO system fed with agricultural leachate blended with well water at 18-25°C. The system operated at 60% recovery with a feedwater of pH 7.1. In this case there was 25 mg/L of PO₄ in the feed. Additionally there was a high level of calcium (565 mg/L) and approximately 200 mg/L of bicarbonate.

6.3.1 Results - This plant has operated satisfactorily without the need for any pH control since February 2006 until the time of writing. There has not been any membrane fouling to date. No cleaning has been necessary to date.

6.3.2 Conclusions - Antiscalant B has been successful in controlling calcium orthophosphate precipitation under these plant operating conditions. The operating limits of this antiscalant have not been reached, and further work may be undertaken to reduce the dosage rate and increase the recovery.

VII. SUMMARY AND CONCLUSIONS

- The effectiveness of antiscalant B as a calcium ortho-phosphate antiscalant has been proven in several RO plants under different operating conditions.

- It is possible to treat not only high phosphate content waters but also to effectively control other scaling species such as iron, calcium sulphate and calcium carbonate with antiscalant B.

- The composition of such an antiscalant as a synergistic blend of organic chemicals allows it to exhibit these multifunctional capabilities.

- The enhanced calcium phosphate inhibition mechanism is through threshold inhibition as the membrane system dynamics rarely result in hydroxyapatite crystal formation.

- It is possible to avoid acid dosage while operating RO plants with high ortho-phosphate feed waters, if a specific phosphate antiscalant is used.

- The effectiveness of the calcium ortho-phosphate antiscalant can be proven in a few days.

- Calcium ortho-phosphate antiscalant does not work in plants with recycle design.

- Calcium ortho-phosphate antiscalant does not avoid colloidal phosphorus deposits, polyphosphates fouling, or organic matter with associated phosphorous.
More studies are needed to see if products like antiscalant B can change the structural morphology within calcium phosphate.

More comparable studies into Calcium phosphate solubility isotherms are required particularly a closer focus on research by osteologists into Calcium phosphate based bone and teeth implant material.

References

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