Innovations in the inhibition and cleaning of reverse osmosis membrane scaling and fouling.

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Abstract:
Scaling and fouling of membranes are an on-going performance issue for most plants This presentation outlines innovations in speciality chemicals designed to inhibit membrane scaling and fouling and to clean membranes where deposition has occurred.

High phosphate waste water reuse RO plant – There is an increasing trend to treat recycled waste water and use it as a feed supply to RO plant. High levels of phosphate can cause rapid scale formation in the membranes. This paper discusses phosphate chemistry and field trails of a new antiscalant which overcomes acid dosing.

Sulphate removal membranes – Specialised nano-filtration membranes have been developed for the removal of sulphate from seawater in offshore wells reducing scale formation and souring in the well-head. The membranes are subject to barium/ strontium sulphate scaling. This section discusses the processes and products to inhibit scale formation.

Removing clay from membranes – Clay is a common place foulant and very difficult to remove from membranes. This section of the paper describes the mechanisms and products developed to effectively remove clay. A number of case studies are described.

Keywords: reverse osmosis, membrane, scaling, fouling, cleaning, chemicals, antiscalant, waste water, reuse, reycle,phosphate, calcium phosphate, sulphate removal, SRP, barium sulphate, strontium sulphate, SR90, clay cleaning, aluminium silicate, hydroxyapatite.

1) INTRODUCTION

There has been a dramatic increase in the number of reverse osmosis and nano-filtration plant over the past ten years. There has also been a proliferation in the variety of feed sources used, including seawater, surface waters and, increasingly, effluents of varying qualities. Not surprisingly, therefore, is the parallel increase in the degree of scaling and fouling, resulting in the need for not only novel preventative antiscalant products in the field, but also new and improved cleaners where deposition has occurred. An essential part of the ability to correctly select and apply the most appropriate products lies in the development of laboratory analysis and predictive tools. This paper presents some innovative products and techniques developed by Genesys International Limited.

2) HIGH PHOSPHATE WASTE WATER REUSE REVERSE OSMOSIS PLANTS

Background - 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.

Issues – There is an enormous recent increase in the number and size of waste water reuse reverse osmosis projects in the last 5 -10 years. Major projects include 325,000m^3/day at Sulabaiya in Kuwait, 263,000m^3/day NEWater project in Singapore at Bedok, Kranji, Seletar and Ulu Pandan and 100,000m^3/day in ten operational plants in Australia. An additional 200,000 m^3/day project has been approved in Queensland Australia. More plant are projected for the future as there is an environmental duty of care to treat waste water and also a significant cost benefit of doing so. Treated waste water is estimated to be 50% cheaper than desalination of sea water.

Waste water can have elevated levels of phosphate from breakdown of effluent products in tertiary treated sewage and due to detergent and fertiliser treatment in agricultural leachate and run-off waters. High phosphate in the feed water to reverse osmosis plant results in calcium phosphate fouling and poor plant operation. Conventional antiscalants are ineffective at high phosphate and high recovery rates and the only other option has been to dose large quantities of acid to reduce feed pH to below 6.2.

There are further complications in that phosphate is multivalent and takes many different forms with varying solubility. Researchers can not agree on the correct solubility of varying forms so scaling prediction is difficult. Some parallel research by dentists has confirmed results from our laboratories that it is very difficult to form crystalline calcium phosphate. The most common form is as an amorphous deposit.

Innovations – A study was undertaken to research the various forms of calcium phosphate and develop a specific calcium phosphate antiscalant.

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 table 1 below: The majority of calcium phosphate deposits are amorphous and only two forms hydroxyapatite and fluoroapatite take on a crystalline structure as shown in figures 1 and 2 .

Chemical Name	**Formula**	**Abb. Name**	**Mineral Name**	**Structure**	**Solubility Product mol/litre**
Amorphous calcium phosphate rock	$Ca_9(PO_4)_6$	ACP		Amorphous	
Monocalcium phosphate	$Ca(H_2PO_4)_2$	MCP			
Dicalcium phosphate dihydrate	$CaHPO_4 \cdot 2H_2O$	DCPD	Brushite	Amorphous	2.32×10^{-7}
Dicalcium phosphate	$CaHPO_4$	DCP	Monetite	Amorphous	1×10^{-7}
Tricalcium phosphate	$Ca_3(PO_4)_2$	TCP	Whitlockite	Amorphous	2.07×10^{-33}
Tetracalcium phosphate	$Ca_4O(PO_4)_2$	TTCP	Hilgenstockite	Amorphous	
Pentacalcium hydroxylapatite	$Ca_5(PO_4)_3(OH)$	HAP	Hydroxyapatite	Hexagonal	2.34×10^{-59}
Pentacalcium fluoroapatite	$Ca_5(PO_4)_3(F)$	FAP	Fluoroapatite	Hexagonal	3.16×10^{-60}
Octacalcium phosphate	$Ca_8(HPO_4)_2(PO_4)_4$	OCP			2×10^{-49}
Calcium pyrophosphate	$Ca_2P_2O_7$	CPP			

Table 1 : Various forms of Calcium orthophosphate

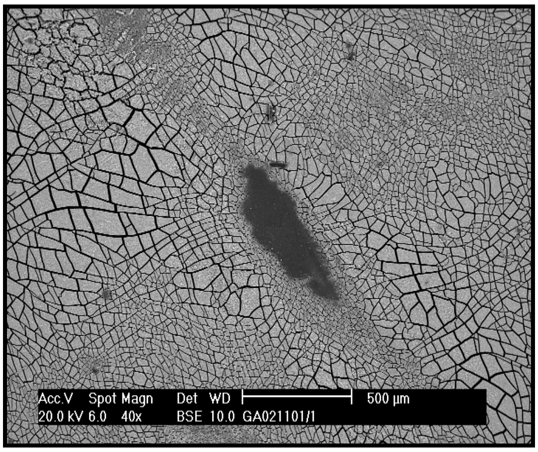

Figure 1 Amorphous calcium phosphate deposit.

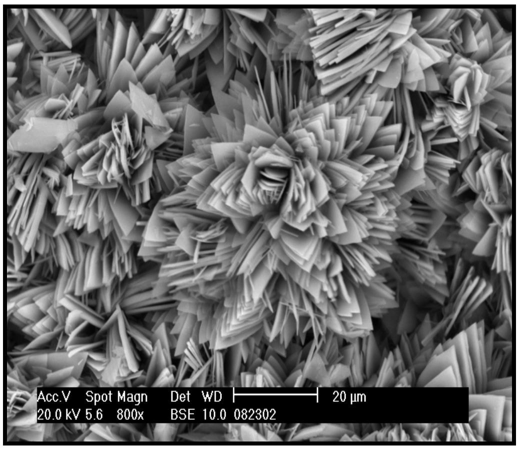

Figure 2: SEM picture and EDX spectrum of probable hydroxyapatite crystals.

Having identified the structure of calcium phosphate, threshold tests for different antiscalant blends were conducted in the laboratory. Commonly used chemicals that distort crystals were replaced with polymeric compounds that showed a high threshold inhibiting effect against calcium phosphate. A product capable of exceeding the % saturation point by over 100 times was developed and called Genesys PHO. The development product has been extensively field trialled and results of one site are shown below.

Field Trial 1 – this waste water re-use plant in Alicante was fitted with ultrafiltration membranes followed by reverse osmosis membranes. Key parameters are shown in the table 2 below.

Cations	**mg/l**	**Anions**	**mg/l**
Calcium	160	Sulphate	290
Magnesium	50	Chloride	440
Sodium	270	Bicarbonate	400
Iron	0.05	Nitrate	0.5
pH	7.1 – 7.7	Silica	10-15
TDS	1700	Phosphate	15 - 25
Feed Pressure	10 Bar	Product Flow	132m³/day
Recovery Rate	75%	Feed Flow	176 m³/day

Table 2: Field Trial 1 key parameters

In one of the pilot trials the RO plant was run with acid dosing to a pH of 7.0 to try and control calcium phosphate fouling. The plant ran initially with a conventional antiscalant C. After a period of two weeks the feed pressure had to be increased from 7 to 10 bar to maintain a constant product and feed flow rate. This was due to calcium phosphate fouling which resulted in an acid clean being carried out one month. A second clean was carried out after a further ten days and feed pressure continued to rise to maintain a constant flow. After two months another conventional antiscalant was tried but rapid fouling occurred after one week requiring a plant shut down and acid clean. The specific calcium phosphate antiscalant Genesys PHO (Antiscalant B) was then used. Initially the pH was lowered to 6.1 and 3.0 mg/l of antiscalant added. The acid was gradually reduced and stopped with pH fluctuating between 7.1 and 7.7. The Genesys PHO dose rate was then gradually reduced to 2 mg/l. During this period constant feed pressure and constant product and feed flow was maintained. On one occasion the plant had an unscheduled shut down for 4 days because of an interruption in electricity supply and the membranes were not flushed. Under theses super saturated conditions hydroxyapatite formed and an acid clean was required. The graphs in figure 3 and 4 demonstrate these results.

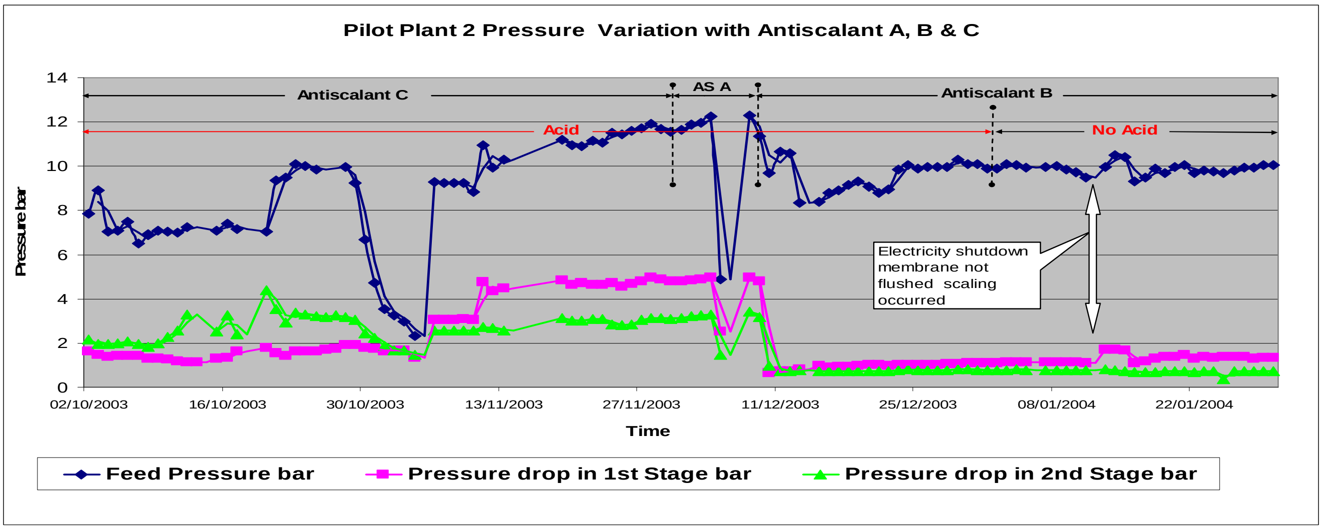

Figure 3: Pressure variation with different antiscalants.

Additional trials have resulted in operational plant running without acid and 2 – 5 mg/l of antiscalant Genesys PHO successfully for over two years without any acid cleaning. An RO Plant in Murcia which is supplied with agricultural leachate water with o-phosphate levels of up to 100 mg/l and 280 mg/l of Calcium has operated without cleaning for 24 months with dramatically reduced acid dosing from pH 6.6 to 7.2. Another agricultural leachate plant whose feed water was blended with Well water operated without any acid dosing at a pH of 7.1, 25 mg/l of o-phosphates, 565 mg/l calcium and a dose rate of 4 mg/l of Genesys PHO. There have been no acid cleans for 22 months.

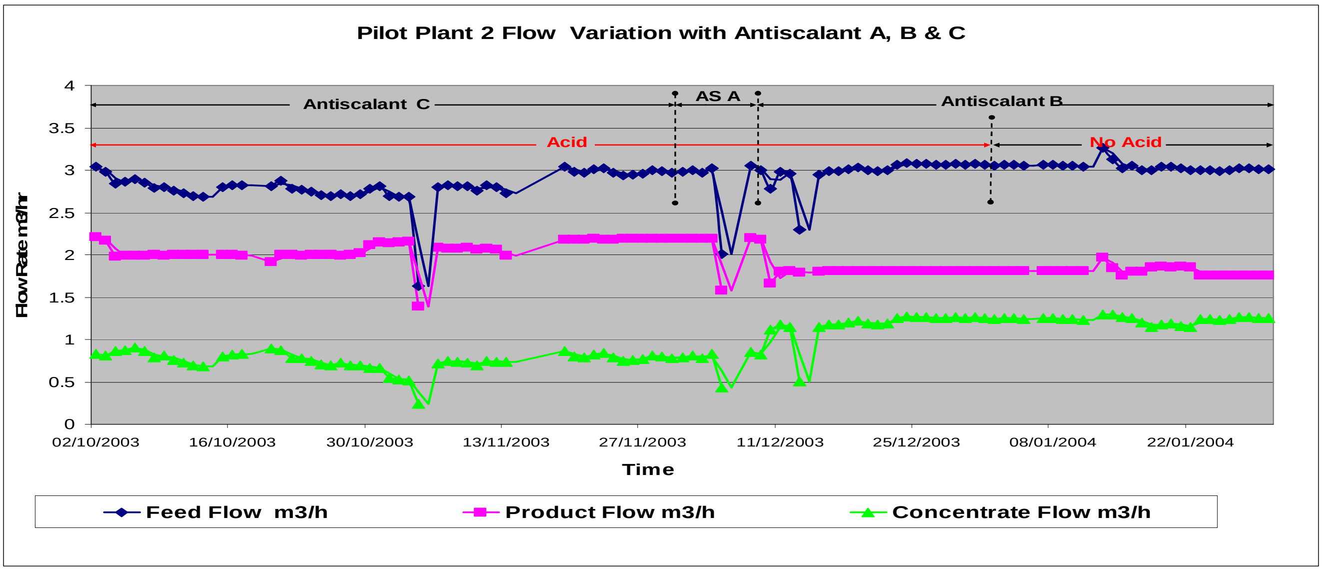

Figure 4: Flow Variation with different antiscalants

The results above and expanded on by Chesters, Darton and del Vigo [1] show that using a highly active threshold inhibiting antiscalant Genesys PHO at a low dose rate of 2 -5 mg/l can increase the solubility of calcium phosphate one hundred and fifty times. This means that there is a solution to operating waste water RO plant without the dangerous practice of dosing very large quantities of acid.

3) SULPHATE REMOVAL MEMBRANE TREATMENT

Background

Sulphate reduction technology was developed jointly between Marathon and Dow from 1987 onwards for the North Sea offshore platforms. Sulphate removal membranes have been developed specifically by DOW FilmTec with the goal of improving oil recoveries by the prevention of barium and strontium sulphate scale precipitation. The Nanofiltration SR90 membranes are themselves subject to scaling and require a specific antiscalants that is compatible with these particular membranes. Figure 5

Figure 5: Offshore SR90 membrane plant.

Issues - When normal high sulphate seawater is injected into reservoirs which have formation water containing barium and strontium, mixing occurs forming a supersaturated barium and/or strontium sulphate solution. If pressure decreases in and around the production wells, the supersaturated barium and/or strontium sulphate solution is no longer stable and precipitation occurs, causing scale formation in the production tubing and / or plugging of reservoir rock around the production well. Petroleum reserves are often lost. In deep water and other complex oil developments, sulphate removal, and the subsequent prevention of scale, provides significant cost advantages. In addition by removing the sulphate in the injected seawater, there is a reduced source of sulphur that can be converted to hydrogen sulphide by thermophilic sulphate reducing bacteria. Consequently, well souring does not occur. There are an increasing number of sulphate reducing platforms notably in Angola, Brazil and the North Sea.

Innovations – Genesys has developed a specific antiscalant Genesys DW (Down Well) which inhibits common scalants and specifically barium and strontium sulphate in the membranes. Barium and strontium sulphate are needle shaped crystals. The scale can be removed with alkaline chelants but the needles readily pierce the membrane surface causing irreparable damage. (Figure 6)

Figure 6: Barium Sulphate crystals

The product is also an excellent iron sequestrant. Genesys DW has been tested for compatibility with the Filmtec SR90 Nano-filtration membranes and received a compatibility statement in December 2005. It is also has authorisation for use offshore in North Sea oil and gas industry from "The Centre for Environment, Fisheries & Aquaculture Science" (CEFAS) and is listed on the "Offshore Chemical Notification Scheme" (OCNS). The product acts as a threshold inhibitor reversing the ordering of protonuclei into nuclei which results in precipitation, as shown in Figure 7 below.

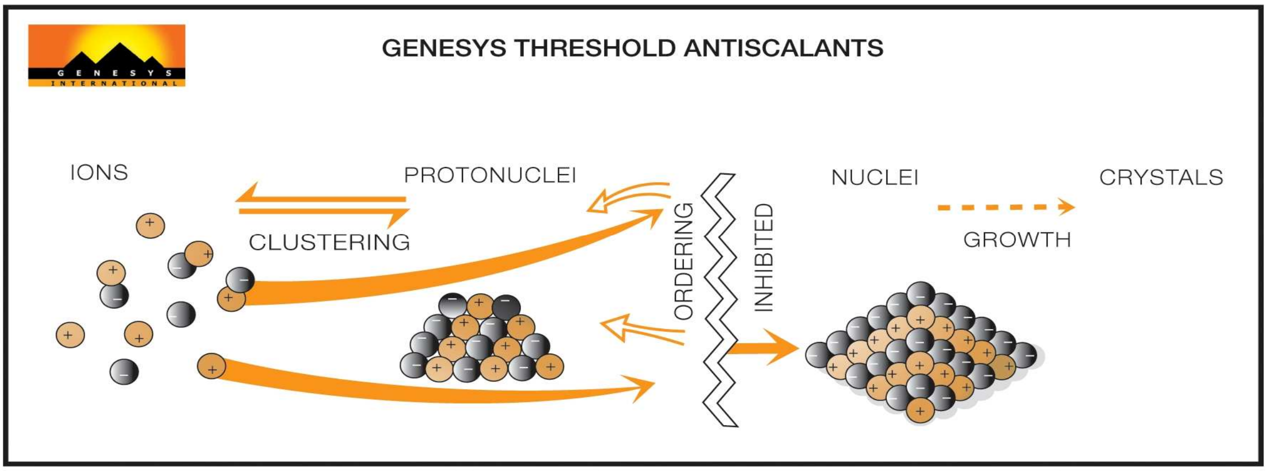

Figure 7: Threshold Inhibition mechanism

The use of Genesys DW protects sulphate reducing membranes from barium and strontium sulphate scale formation and iron fouling thus prolonging the lifespan of the membranes.

3) REMOVING CLAY FROM MEMBRANES

Background – The Genesys laboratories in Madrid found that over 5 years the most frequent foulant in the lead element of RO plant was alumino-silicates or clay as shown in figure 8. Clay comes from surface waters, rivers and reservoirs but also can find it's way into any RO plant feed water system. Pre treatment to remove clay is rarely a 100% efficient process.

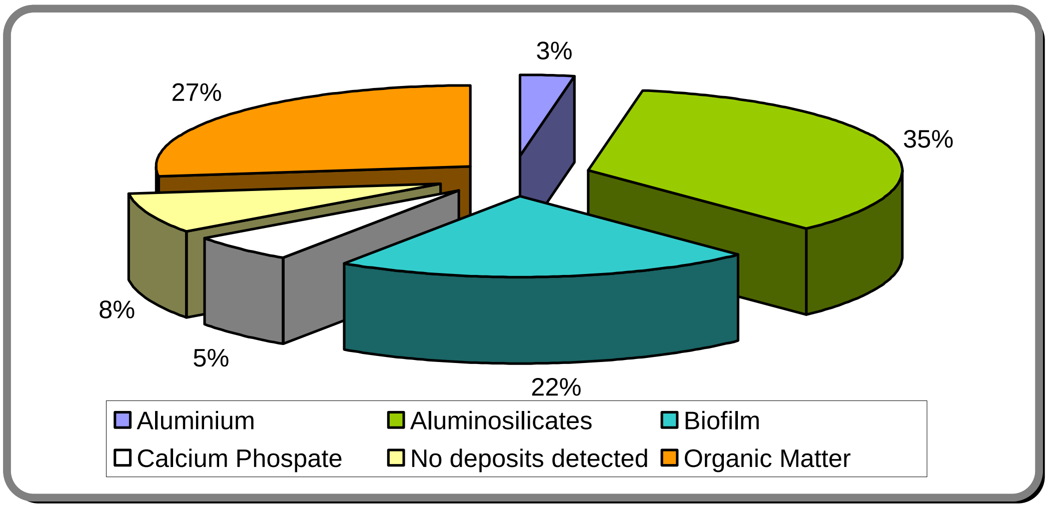

Figure 8: Main types of foulant found on membrane elements in first position during autopsy (2001-2005).

Issues – Clay is made up of alumino-silicates and is colloidal. It attaches to the membrane surface rapidly and causes reduction in flux and increase in feed pressure as the permeability of the membrane is reduced. The membrane surface becomes covered in an impenetrable mat as shown in Figure 9.

There are several alumino-silica formulations:

Clay:	$Al_2O_3SiO_2.xH_2O$
Kaolin (china clay)	50% Al_2O_3 : 55% SiO_2
Feldspar	KAl SiO_3
Mullite	$3Al_2O_3.2SiO_2$
Andalucite	Al_2OSiO_4

Figure 9: clay on membrane surface

Clay deposits are often associated with iron and microbiological fouling and are difficult to remove from membrane surfaces using conventional acid and alkaline cleaners.

Innovations – a new powdered clearing compound was developed and tested in the laboratory. Genesol 703 is based on high pH phosphate cleaners with a chelant and surfactant. This combination of products has a detergent and surfactant effect on the colloidal foulant and the high ionic strength created at the membrane surface allows osmosis to occur at the membrane boundary layer helping lift deposits from in and around the membrane pores. Laboratory tests showed this product to be much more effective than conventional cleaning products. The product has recently received NSF approval for use in drinking water RO plants.

CASE STUDY - SEM and EDAX analysis showed the membrane in figure 10 to be fouled with iron oxide & aluminium silicate. Samples of membrane were placed in a flat sheet test rig figure 11 and combinations of cleaning solutions were used to ascertain the preferred cleaning method. The results after each stage of cleaning are shown in Table 3 below. Figure 12 shows the sample of cleaned membrane.

Cleaning Method	Flow @ 25° C Design = 45.05 L/m2/h	% salt rejection Design 99-99.5%
Cleaning 1: 3% Genesol 38 for 1 hour ambient	39.26	99.1
Cleaning 2: 2% Gen 34 + 1% Gen 36 (2h) at 35 C	42.95	99.4
Cleaning 3: 2% Genesol 40 (2 h) at 35 C 3% Genesol 38 (1 h) ambient 2% Genesol 40 (2 h) at 35 C	44.97 40.63 44.39	99.1 99.2 99.3
Cleaning 4: 1% Genesol 703 (2 h) at 35 C 3% Genesol 38 (1 h) at 35 C 1% Genesol 703 (2 h) at 35 C	45.5 40.74 46.97	99.4 99.3 99.3

Table 3: Results of cleaning test methods

Figure 10: clay fouled membrane

Figure 11: Flat sheet test rig

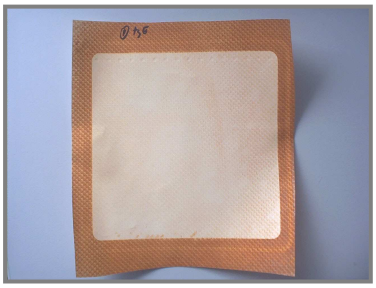

Figure 12:Clean membrane sample

A combination of Genesol 703 to remove microbial fouling and clay alternated with a mild acid wash to remove iron deposits restored this badly fouled membrane to its design parameters.

Conclusions – in order to support the world's requirement for clean pure water there has been a necessary acceptance of reverse osmosis technology. Innovations in engineering and a desire to minimise environmental impact by optimising plant performance has resulted in new challenges to maintain membrane performance and longevity. This paper has identified a number of new antiscaling and fouling speciality chemicals and techniques to improve plant operation.

- Waste water reuse/recycling reverse osmosis plant can operate without having to dose large quantities of acid to reduce feed pH to control calcium phosphate scale by using a new antiscalant Genesys PHO, which uses advanced threshold inhibiting mechanisms to raise the solubility of calcium phosphate 150 times.
- Barium and strontium sulphate scale formation can form in off-shore oil rigs using SR90 membranes for sulphate removal. Genesys DW is a new antiscalant designed to prevent all forms of scale formation and iron fouling whilst being compatible with the nano-filtration membranes.
- Clay fouling of a reverse osmosis membrane has historically resulted in failure and replacement. A new powdered high pH cleaner Genesol 703 has shown to be effective in clay removal through a combination of detergent and surfactant mechanisms combined with osmosis from the permeate to the concentration boundary layer which assists in dislodging particles.

References:

[1] Chesters, S. P., Darton, E.G., Vigo, F.D., Theoretical and practical experience of calcium phosphate inhibition in RO waters. *IDA World Congress Desalination and Water Reuse Gran Canaria October 2007*