

Cost saving case study using a calcium sulphate specific antiscalant.

Authors: Stephen.P. Chesters, Matthew.W. Armstrong, David A. Golding, Hussain Ostovar.

Presenter: Stephen P. Chesters, Managing Director Genesys International Ltd. UK

ABSTRACT

Extensive extraction from aquifers often leads to deterioration in water quality. This is usually seen as an increase in the soluble salt levels which, over time, has a detrimental effect on membrane performance. A limiting factor in the efficiency of membrane operation is the recovery rate that can be achieved, particularly with 'brackish' water operation. A high recovery rate causes an increase in the concentration of salts in the reject water. Eventually the solubility product of some of the scaling species is exceeded resulting in salt precipitation and scale formation.

The availability of antiscalants that are specifically designed to be active against individual scaling species is essential to allow the economic operation on increasingly challenging feed waters. Deep well extraction of groundwater often results in waters with a high level of sulphate ions. This paper describes the chemistry and morphology of calcium sulphate scale and its formation mechanisms. Calcium sulphate scale crystals occur naturally in three forms, anhydrite CaSO_4 , hemihydrate $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (plaster of Paris) and the dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Under the temperature conditions of membrane operation the dihydrate form occurs as blade like crystals that can damage the membrane surface. Cleaning is rarely successful making calcium sulphate one of the most damaging scaling species.

The processes involved in the development of the new calcium sulphate specific antiscalant "Genesys CAS" are outlined and its performance within a complex brackish water RO system with brine recovery is described. The plant had previously suffered from calcium sulphate scaling and membranes had to be frequently cleaned, and their overall performance declined sharply. The satisfactory use of a sulphate specific antiscalant resulted in the overall plant recovery rate increasing from 48% to 61%. Using the membrane manufacturer's software, pump energy savings were calculated based on the increased recovery. These savings, combined with a rationalisation of chemical use and increased membrane life are used to provide a model of overall cost saving.

This case study is the first in a series of three papers covering sulphate, silica and phosphate specific antiscalant development and field-trial performance.

I INTRODUCTION

More than twice as many brackish water RO plants than sea water plants have been built since the first units were commissioned in the late 1960's. In recent years the desalination industry has focussed on increasing the huge sea water RO systems being installed around the world, and innovations in this area tend to capture the news headlines. The high salinity of seawater means that desalination using membrane systems requires feed pressures of 50-70 bar. This compares with lower salinity feed water sources that can operate at 10-20 bar in the case of brackish and recycle waters. High pressure operation requires more expensive equipment and associated higher operational costs.

Over the last eight years production capacity of 9×10^6 M³/day has come on line using "brackish" water from lakes, rivers, aquifers, industrial waste water, sewage effluent, leachate and agricultural run-off . This is significantly more than the increased capacity of 7×10^6 M³/day from sea water installations over the same period. In brackish water operation a limiting factor in efficiency is the percentage of product water recovered from the feed stream; this is determined largely by the feed water quality. As the recovery rate increases the concentration of dissolved salts in the reject water stream increases and it becomes likely that the solubility product of the some of the scaling species will be exceeded leading to salt precipitation and scale formation.

This paper the first in a series of three, examines the use of a new antiscalant formulation developed specifically to inhibit calcium sulphate precipitation in membrane systems. The chemistry and deposition mechanisms are discussed as are the results from an operational plant which shows a significant improvement in performance. This case study is used to determine the operational cost savings achieved by the use of speciality products that enable recovery rates to be enhanced. Capital costs can also be reduced if the system designers are confident enough to 'design' system operation at higher recovery rates.

II CALCIUM SULPHATE

The three major forms of calcium sulphate, hemihydrate, dihydrate and anhydrate have differing solubility isotherms as shown in figure 1. For RO waters the anhydrate form predominates. The solubility of calcium sulphate, in the dihydrate form ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ gypsum) is similar to calcium carbonate which decreases with increasing temperature. However whilst the precipitation of calcium carbonate scale can often be minimized by reducing the pH of the feed water, calcium sulphate solubility is independent of pH.

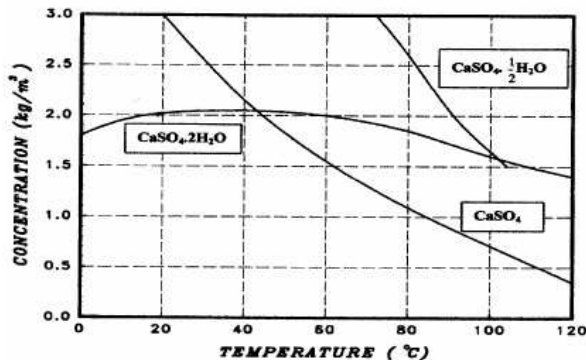


Fig 1: Solubility of forms of calcium sulphate

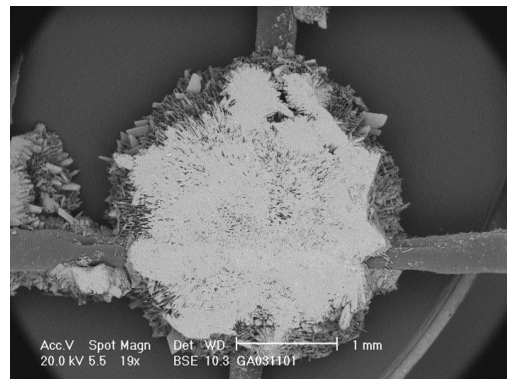


Fig 2: Rosette formation on spacer

It is reported in literature Gouellec et al [1] that gypsum scale forms via lateral growth of crystals directly on the membrane surface as well as the deposition of crystals onto the membrane surface. Studies in the Genesys laboratory in Madrid frequently shows crystal platelets forming in the low flow cross over points of the feed spacer – see fig. 2. This feature is further demonstrated when the spacer is removed from the membrane surface during autopsy and it becomes clear the scale is deposited within the spacer layer rather than at the underlying membrane surface. Studies by Rahardianto et al indicated a variation in scale formation due to varying surface topology of different membranes [2]. Scale formation occurs initially in needle form developing into platelets and rosettes. The scale is frequently damaging to membrane surfaces through particulate abrasion and is difficult to remove with chemicals. The development of calcium sulphate scale in the membrane can be further complicated by the potential for precipitation to occur before water concentration along the membrane surface. In these cases an amalgam of partially formed crystals can form. Ben Ahmed et al investigated the effects of different antiscalant compounds showing that phosphonate compounds inhibited the germination of scale crystals and polyacrylic compounds acted as dispersing and crystal distortion agents [3].

III ANTISCALANT DEVELOPMENT

All antiscalants work at a sub-stoichiometric level by one or more closely inter-related mechanisms of threshold inhibition, crystal distortion and dispersion. Chelation is also a mechanism for scale inhibition although taking place at the stoichiometric or molar ratio level.

3.1 Threshold inhibition – prevents the precipitation of salts once the salt has exceeded its solubility product. The chemical inhibitors retard or delay the clustering process of charged ions and protonuclei. The most effective threshold inhibitors are based on phosphonic acids (or their salts) which have the added advantage of sequestering iron in a stoichiometric reaction. This is important in membrane applications as any soluble iron will cause rapid fouling as it oxidizes and becomes insoluble. In the water treatment industry there a number of commonly used phosphonates which have different structures and properties that influence their ability in retarding precipitation of the different scaling species. Four of the more common molecules with typically molecular weights of 200-300 are:

HEDP	1-hydroxyethylidene 1-1- diphosphonic acid
AMP/ATMP	aminotri(methylenephosphonic acid)
PBTC	2-phosphonbutane-1, 2, 4-tricarboxylic acid
PPCA	polyphosphinocarboxylic acid (higher MW ~1000+)

3.2 Crystal Distortion – chemicals affect the ordering and growth reactions of crystals causing an irregular shape and weak structure. Chemicals with effective crystal distortion properties tend to be polymers of low molecular weight 2,000-5,000. Many of these polymers exhibit some threshold effectivity whilst others (of higher MW) have dispersing properties. Importantly, many of these ‘polymers’ are ineffective at preventing iron deposition as they tend to react with iron to produce iron acrylate which often damages the membrane surface. The most commonly used products are:

PAA	Polyacrylic acid
PMA	Polymaleic acid
PCA	Polycarboxylic acid
PAMAMS	Polyaminoamide dendrimers
CMI	Carboxymethylinulin

3.3 Crystal Dispersion – occurs when the inhibitor chemisorbs onto the crystal surface and imparts an additional surface charge causing repulsion and ultimately dispersion. Although the growing crystal needs to be enveloped in a polymer of high MW 20,000-40,000 to gain a significant surface charge, the lower MW polymers used for crystal distortion can also put a weak charge on the precipitated salt; this can usually be measured by Zeta potential. Few of the antiscalants used in the membrane industry utilise polymers of a sufficiently high molecular weight to cause chemisorption on to crystal surfaces.

3.4 Formulation – Following an analysis of the chemistry, formation, dynamics and kinetics of the specific scaling species some potentially active ingredients were chosen, combined into formulations and then tested against known standard performing antiscalants to see if an improved performance could be observed. [3] Specific areas of interest for inhibiting calcium sulphate scale are summarised in table 1 below.

species	crystal form	kinetics	position	seeding agents
calcium sulphate	monoclinic prisms, needle & platelets	slow	last element	colloidal calcium sulphate

Table 1: Properties of sulphate scale

Based on observations shown in table 1, certain assumptions regarding molecules that have differing properties can be made. Calcium sulphate is a strongly crystalline salt that develops through weak needle and platelet forms to highly stable rosettes particularly in low flow areas in the membrane feed spacer. It may be concluded that slow kinetics of precipitation particularly in the cross-over fabric of the spacer material indicates slow water velocity and the breakdown of the ‘threshold property’.

It has been theorised by Darton [4] that in the case of ‘threshold inhibitors’ used in laboratory studies in standard threshold tests, the more antiscalant added to the water the longer the time to the onset of precipitation. In all cases some minor precipitation occurs and this eventually leads to ‘catastrophic precipitation’ where the precipitating salt reaches equilibrium and there is no enhanced solubility at all. Eventually all threshold performance is lost, irrespective of the treatment levels used.

Consideration of these laboratory phenomena enabled combinations of threshold inhibitors, crystal distortion and dispersion agents to be used in a formulation to build a more effective calcium sulphate antiscalant.

3.5 Threshold testing – is conducted by preparing standard solutions of specific scaling salts. The antiscalant formulations under test are added at different dose rates and the solution agitated at 25°C using variable contact times. The samples are filtered and the filtrate analysed for the presence of the scaling species. The % threshold inhibition can be determined as the percentage of scaling species that

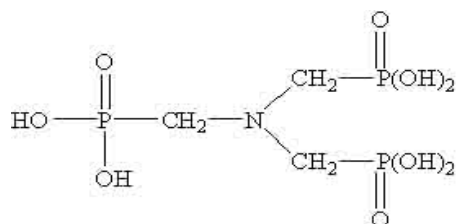


Fig3: Sodium phosphonate molecule

remains in solution. Further tests are conducted using the most effective formulations with different operating pH, temperature and incubation times. Finally, tests are run against all common scaling species so that the final formulation has a broad spectrum of activity whilst being highly effective against a specific scalant. A sodium phosphonate compound Figure 3 was used for general nucleation inhibition. Growth of scale proto-crystals are disrupted and re-dissolved. This compound is commonly used in water

treatment chemicals and is particularly effective against calcium carbonate operating at a Langelier Saturation Index of +2.6. Research and laboratory threshold testing revealed that a potassium salt of a methylene phosphonic shown in Figure 4 showed a propensity to specifically inhibit calcium sulphate scale formation. The molecule disrupts the ordering process of proto-nuclei thus inhibiting precipitation.

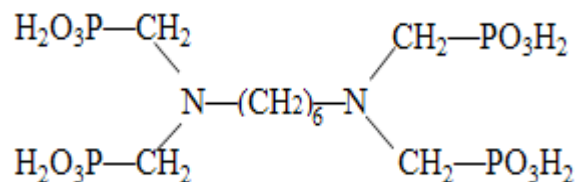


Fig4: Methylene phosphonic molecule

This molecule is the main component of the calcium sulphate antiscalant. The effectiveness of the product was found to increase when organic dispersants and a crystal growth inhibitor based on a phosphino carboxylate and a polyacrylic acid with a molecular weight of ~ 2,000 were included in the formulation.

IV CALCIUM SULPHATE CASE STUDY

A chemical manufacturing company 180 km east of Tehran, Iran commissioned a 7,000 m³/day two pass brackish water RO plant with brine recovery in September 2005. The system is a complex arrangement of 3 R.O. streams, each with pre-treatment (see Figure 5). The design consists of a first pass with two identical skids of two stages in 20:10 array, each pressure vessel having 6 membrane elements. Both skids (RO1A and RO1B) have a design permeate flow of 143 m³/hr at 63.5% recovery to give a total 1st pass production of 286 m³/hr. Hydranautics CPA 3 membranes are installed in both skids. Pre-treatment for the first pass consists of aluminium salt coagulant, hydrochloric acid injection, (to reduce the feed pH) and chlorination, followed by multi-media filtration. A broad spectrum phosphonate based antiscalant had historically been dosed after the multi-media filters together with sodium metabisulphite, (SMBS) which is added to de-chlorinate the feed preventing membrane oxidation. The 2nd pass RO2 is designed to operate at 85% recovery and is fitted with Hydranautics CPA4 membranes. The 2nd pass permeate is high quality water for boiler feed and process use. The reject from the 2nd pass is returned back to the 1st pass feed stream downstream of the cartridge filters.

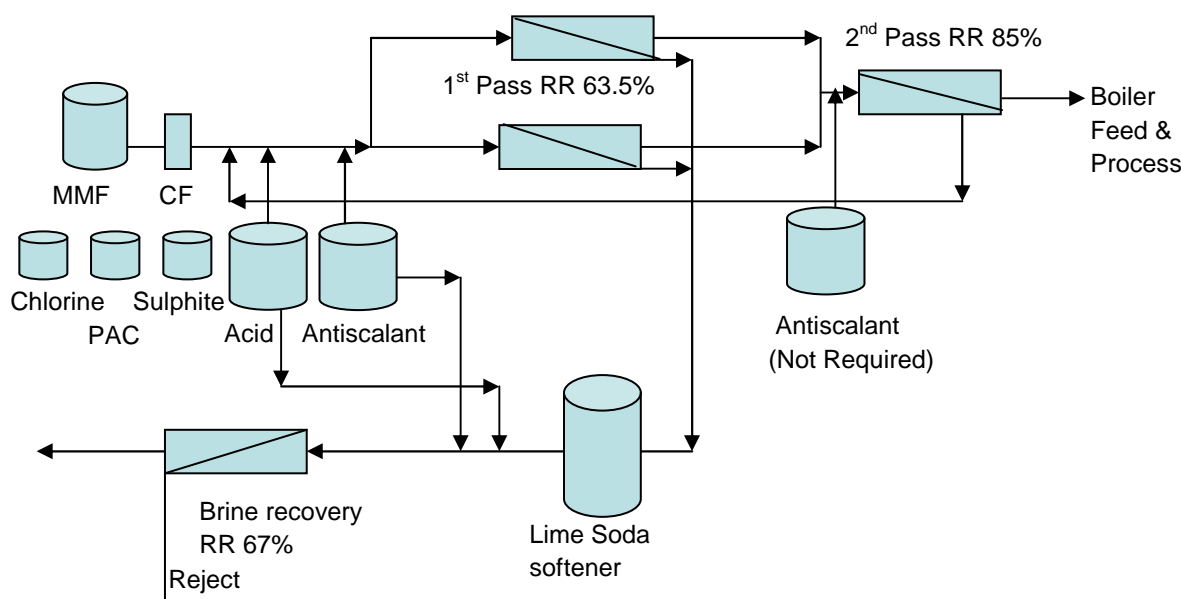


Fig 5: Schematic of plant layout

Concentrate water from the 1st pass is sent for treatment via a Brine Recovery R.O. (BRRO). The theoretical conductivity of this water would be around 20,000 μScm^{-2} with extremely high concentrations of scale forming salts. To allow further processing it is first treated by addition of lime and soda ash in a clarifier to reduce hardness and remove a proportion of other elements such as silica, although there is little effect on sulphate removal. After softening and filtration, a conventional broad spectrum antiscalant is dosed and the water passes to the BRRO, operating at 67% recovery.

The raw water derives from underground wells. The chemical water analysis from September 2007 shows (as ions) calcium of 785 mg/l, sulphate at 2,149 mg/l and bicarbonate of 141 mg/l with a pH 7.5 and TDS 4,745 mg/l. The use of scaling prediction software showed that calcium carbonate, calcium sulphate and barium sulphate salts all exceeded their solubility limits. The use of a standard antiscalant could inhibit calcium carbonate and barium sulphate but not calcium sulphate at these high values.

The first pass trains A & B of the plant historically suffered from calcium sulphate deposition. Consequently the operators decided to reduce recovery rates to 48% against a design specification of 63.5%. Even at lower recovery rates the membranes fouled after 4 – 5 weeks of operation with feed pressure increasing from 10 to 12.5 bar. Attempts were made to clean the membranes again but in many instances they had to be replaced. Cleaning was carried out when ΔP reached 6.5 Bar and when feed pressure reached 12.5 Bar. Cleaning was attempted by circulating a solution of Ethylene Diamine Tetra Acetic acid, (EDTA) and Sodium TripolyPhosphate, (STPP) at high pH. After flushing to remove the cleaning solution, there was a reduction in ΔP , with a consequent reduction in feed pressure to achieve the desired permeate flow. If conditions were changed to increase the permeate flow it is expected that ΔP would rise back to near 6.5 Bar necessitating increasing the feed pressure to 12.5 bar. We suspect there is a residual fouling which is not being removed by this cleaning causing the increase in ΔP . However, flux rates did improve and so the cleaning had successfully removed some foulant from the membrane surface but not from the feed/brine channel. Immediately after cleaning, 1st. Stage ΔP decreased to around 5.5 Bar, but this would subsequently rise with increasing feed pressure until reaching ~6.5 Bar after four weeks. The maximum operational ΔP , as recommended by the membrane manufacturer is 3.5 Bar and the maximum excursion limit is 4.1 bar and beyond these limits, membrane damage can be expected.

The membranes from the concentrate side of the plant which could not be cleaned were all moved into RO1B which operated with a reduced permeated flow of 59m³/hr. A conventional antiscalant had been used combined with acid dosing to reduce pH from 7.5 to 7.1. This required 132 kg of 35% hydrochloric acid per day at an estimated cost of \$19,200 per year. Chlorine dosing to oxidise iron and control microbiological growth required sodium meta bisulphite neutralisation of the chlorine prior to the membranes. The resultant low pH product water was dosed with sodium hydroxide to raise the pH. The second pass is fed with permeate from the first pass operated at an 85% recovery design value without any problems as there are only low level of scaling species in the feed water.

The brine recovery system had high levels of sulphate >5,400mg/l on the feed which were not removed by the lime soda clarifier. The calcium levels were only partially reduced from over 2,000 mg/l in the reject of the first pass to 495 mg/l in the feed to the BRRO. This plant rapidly scaled and could not operate with these high levels of sulphate and a conventional antiscalant. The plant was therefore moth-balled until cost effective technology in the form of mechanical engineering or improved chemistry became available.

4.1 Recommendations

In November 2007 the new calcium sulphate specific antiscalant was introduced and acid dosing was stopped. At 4.7 mg/l dosed to the feed water this approach has successfully prevented scale formation, and the recovery rates were gradually increased to 61%; the plant requiring only one membrane clean in 18 months instead of one every month as previously. The second pass permeate polisher is operating without the need for antiscalant due to the good quality permeate from the first pass.

Apart from the first pass operating nearer to its original design specification the brine recovery system (BRRO) is now operable at 67% recovery at 131 m³/hr; this is a huge benefit to the economics of the system overall. The acid dosage was stopped as the calcium carbonate saturation index was not exceeded at a pH of 7.5 and any additional acid usage had no effect on reducing calcium sulphate saturation. With the acid dosing removed from the feed water sodium hydroxide addition to the permeate is no longer needed. The aluminium based coagulant has also been replaced with a polyamine based cationic flocculant which has reduced the SDI in the feed from 3.0 - 7.0 to consistently less than 3.0. This in turn has helped the effectiveness of the lime soda softener. The groundwater well has a low level of microbiological activity so the chlorine dosage has also been removed along with the sodium metabisulphite chlorine neutraliser. Simplifying the chemicals used on the plant has both operational and economic benefits; the system works much better and at significantly lower cost.

4.2 Results and Cost Savings

The selection of a speciality antiscalant has resulted in significant costs savings and a more efficient plant with less complex chemical dosing regime. Some of the water savings are shown in table 2 below.

4.2.1 Water – the increased recovery rate allows constant desired permeate production with reduced feed water requirements. Table 2 shows that by increasing the recovery from 48% to 61% savings in precious ground water resource amount to over a million tons per year. At the same time the concentrate stream which makes up the effluent discharge from the plant is also reduced significantly by the same amount.

	Permeate m ³ /hr	Feed m ³ /hr @ 48% Recovery	Feed m ³ /hr @ 61% recovery	Feed Saving m ³ /hr	Feed Saving m ³ /annum
Skid A	143	298	234	64	560,640
Skid B	143	298	234	64	560,640
TOTAL	286	596	468	128	1,121,280

Table 2: Feed water savings on 1st pass skid

4.2.2 Energy Costs - The water saving by increasing recovery can be translated into an electricity cost due to reduced feed water pumping. Using the latest Hydranautics IMSDesign RO Projection Programme the KwHr/m³ pump energy demand can be calculated for different operating conditions. In November 2003 the original design specification was for each skid to produce 143m³/hr of product water operating at a recovery rate of 63.5%. In September 2007 Skid A produced 136m³/hr of product water at recovery rate of 48%. The feed flow rate was 283m³/hr which required 0.85KwHr/m³ of pump energy. In November 2007 the membranes were cleaned and the new sulphate specific antiscalant dosed at 4 – 5 mg/l. By February 2008 membrane scaling was being inhibited and recovery rates were gradually increased. As recovery rates increase the feed pressure rises to counter the higher osmotic pressure. Recovery rates continued to increase throughout 2008 without calcium sulphate scale

Skid 1 a	Nov-03 Design	Sep-07	Feb-08	Feb-09
Feed Pressure Bar	12.80	12.50	10.70	12.00
% Recovery Rate	64	48	58	61
Feed Flow m3/hr	225.20	283.00	243.00	228.00
Permeate Flow m3/hr	143.00	136.00	140.00	139.00
Pump Energykwhr/m ³	0.63	0.85	0.58	0.62
Energy KwHr	141.88	240.55	140.94	141.36
Total Energy/annum KwHr	1225808.64	2078352.00	1217721.60	1221350.40
Pumping Costs/ annum	\$85,806.60	\$145,484.64	\$85,240.51	\$85,494.53

Table 3: Electricity cost savings

formation and the plant is now operating close to its design specification. The current pump energy use at 61% recovery rate is 0.62 KwHr/m³. This represents an annual energy saving of USD\$60,000 on this single skid assuming an electricity cost of \$0.07/KwHr. This saving would be doubled if applied to both skids.

4.2.3 Acid dosing – Hydrochloric acid was used to reduce the pH and scaling tendency of calcium carbonate. A reduction of pH from 7.5 to 7.1 required a dose of 132 kg/day of 35% hydrochloric acid. Calcium carbonate scaling can easily be inhibited with an antiscalant and reduced pH has no effect on inhibiting calcium sulphate scale therefore the hydrochloric acid was removed saving 48 tons of acid per year at an estimated cost of \$19,200.

4.2.4 Chlorine dosing – the original design used 0.2-0.5 mg/l of chlorine to reduce microbiological fouling. To retain this residual of free chlorine a daily dose of 86 kg of 12.5% sodium hypochlorite was needed. Sodium bisulphite is dosed prior to the cartridge filter to neutralise any remaining chlorine to protect the membranes from oxidation damage. As the microbial profile of the well water showed a very low level of microbiological activity so the chlorine dosing was removed resulting in an annual saving of around \$15,000. The bisulphate was also removed with an addition saving of \$3,000/annum.

4.2.5 Membrane Element Replacement - Since commissioning in September 2005 it is reported that all of the membranes have been renewed over a two year period. The 270 elements were replaced at an estimated cost of \$162,000. Since November 2007 to February 2009 there have not been any membrane replacements. The membrane lifespan has been increased dramatically and present replacement schedule is estimated to be 70 membranes per year a potential annual saving of \$39,000.

V CONCLUSIONS

The development of speciality antiscalants for different scaling species allows poor quality groundwater sources to be utilised economically, which is an important factor when designing RO plant. The raw water chemistry is a major limiting factor and the correct selection of the most suitable antiscalant can have a huge impact on plant design. The case study discussed above shows that the purpose formulated calcium sulphate antiscalant has allowed the recovery rate of this important installation to be increased from 48% to 61%. A summary of the annual cost savings is shown in Table 4. This is a typical example of the cost savings achievable by using an accurate water analysis and an effective prediction tool.

	Sulphate Case Study
Water Saving, m ³ /annum	1,121,280
Energy Saving, KwHr	857,002 (1 skid)
Energy Costs Saving, US\$/annum	\$60,000
Membrane Replacement, US\$/annum	\$39,000
Chemical saving, US\$/annum	\$37,000
Total, US\$/annum	\$136,000

Table 4: Case Study Cost Savings

This paper demonstrates that the selection of the correct chemical programme and using species specific antiscalants can result in:

- Optimising the recovery rate so as to minimise pumping costs
- Maintaining membrane cleanliness and reducing cleaning frequency
- extending the lifespan of the membranes thereby reducing replacement costs
- Removing the dependency and the cost of dosing large quantities of non specific commodity chemicals which frequently has a positive environmental impact

The use of groundwater as a feed source for RO systems will continue to grow as resources diminish. One of the key limiting factors for RO design and operation is the source water quality. By understanding the various scaling mechanisms and being able to produce synergistic inhibitors improved antiscalants can be targeted against different scaling species. Once tested in the field and laboratory certain development products have become important in ensuring economic and viable operation of RO plant with poor quality brackish water. Calculating pump energy savings with increased recovery is now possible using new software available from the membrane manufacturers. With this information the real cost benefits associated with choosing the correct antiscalant can be defined.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. H Ostovar for his hard work, help and support in compiling the data for the case study reproduced in this paper.

This paper is the first of three exploring the development of sulphate, silica and calcium phosphate specific antiscalants and demonstrating the costs savings that can result.

REFERENCES

- 1 Y.A. Le Gouellec, M. Elimelech, Calcium sulfate (gypsum) scaling in nanofiltration of agricultural drainage water, *J. Membr. Sci.* 205 (2002) 279.
- 2 Rahardianto A. Diagnostic characterization of gypsum scale formation. *Journal of membrane Science* 279(2006) 655-668.
- 3 Ben Ahmed S. et al. / *Desalination* 167 (2004) 311-318
- 4 Amy T. Kan Quantitative Evaluation of Calcium Sulfate Precipitation Kinetics in the Presence and Absence of Scale Inhibitors SPE International Symposium on Oilfield Chemistry, 20-22
- 5 E.G.Darton: Membrane chemical research: centuries apart: Membranes in Drinking and Industrial Water Production. *Proceedings Volume 2*, pp 161 - 171