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Maximising RO recovery using a new antiscalant for high sulphate waters

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ABSTRACT

Despite the current economic turmoil the need for good quality drinking water continues relentlessly. In the last eight years 11,825 reverse osmosis (RO) plants have come on line with a combined output of 25 million m³/d. Although large seawater plants take most of the 'desalination news, awards and headlines', a large number of small and medium sized plants (requiring less energy) are being commissioned that use other water sources. Recent data shows that some 8,500 of these systems are producing 62% of the extra water capacity installed since 2000; these plants use brackish, surface or waste water as a feed source. The increasing demand for the minerals that are found in arid and desert areas has increased the need for desalinated water in many mining areas. In these regions ground waters frequently contain high levels of calcium, magnesium, silica and sulphate; in such cases water desalination increasingly demands sophisticated speciality antiscalants and dispersants. This paper examines the use of new antiscalant compounds developed specifically to inhibit the formation of calcium sulphate. The chemistry and deposition mechanisms are presented along with details of formulating Genesys CAS a sulphate specific antisclant. Results from an operating plant are presented showing the improvement in plant performance and a simple model is developed to equate the improvement in plant operation associated with high recovery to actual cost savings. Membrane systems will continue to be built and operated with increasingly poorer quality feed waters. For this reason it is essential that new and improved speciality antiscalants are developed so that plants can continue to operate at their highest efficiency thereby saving water and energy.

Keywords: Antiscalant; Chemicals; Silica; Calcium phosphate; Calcium sulphate; Brackish water; Recovery rate; Reverse osmosis; Membrane

1. Introduction

More than twice as many brackish water RO plants than seawater plants have been built since the first plants were commissioned in the late 1960's. The desalination industry has focussed recently on increasing the capacity of seawater RO plant and innovations in this area tend to capture the news headlines. RO desalination of seawater requires feed pressures of 50–70 bar, compared with lower salinity feed water sources that can operate at 10–20 bar. High pressure means bigger more expensive equipment and higher operational costs. Over the last eight years production capacity of 9 million m³/d has come on line using "brackish" water from lakes, rivers, aquifers, industrial waste water, sewage effluent, leachate and agricultural run-off waters. This is more than the increased capacity of 7 million m³/d from seawater plants over the same period. A limiting factor of operational efficiency of brackish water RO plant is the recovery rate or percentage of product water recovered

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from the feed stream which is determined largely by the feed water quality at the design stage. A high recovery rate increases the concentration of dissolved salts in the reject water stream and eventually the solubility product of the some of the scaling species is exceeded resulting in salt precipitation and scale formation.

This paper examines the use of new antiscalant compounds developed specifically to inhibit the formation of calcium sulphate in membrane systems. The chemistry and deposition mechanisms are described and discussed. Results from an operating plant demonstrating an improvement in performance are presented. The case study results are used to determine the costs savings achieved by application of this speciality product and consequent increases in recovery rates.

2. Calcium sulphate

Calcium sulphate (gypsum) is similar to calcium carbonate as solubility decreases with increasing temperature. However while the precipitation of calcium carbonate scale can often be minimized by adjusting the water feed (prior to RO desalination) to acidic conditions, calcium sulphate precipitation is insensitive to pH. There are three major forms, hemi-hydrate, di-hydrate and an-hydrate with differing solubility isotherms as shown in Fig. 1. For RO systems we are concerned with the anhydrate form.

It is reported in the literature that gypsum scale forms via lateral growth of crystals directly on the membrane surface and also due to deposition of bulk formed crystals onto the membrane surface [1]. Studies in the Genesys laboratory in Madrid frequently show crystal platelets forming in the low flow cross hair areas of the feed spacer (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. Studies by Rahardianto 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 and is very difficult to chemically remove. The development of calcium sulphate scale in the membrane can be further complicated by the potential for precipitation to occur before concentration in the membranes. In these cases an amalgam of partially formed crystals can deposit on the membrane. Ben Ahmed et al. investigated the effects of different antiscaling compounds showing that phosphonate compounds inhibited the germination of scale crystals and polyacrylic compounds acted as dispersing and crystal distortion agents [3].

3. 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.

3.1. Threshold inhibition

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 sodium salts of phosphonic acids which have the added advantage of sequestering iron in a stochiometric reaction. This is vital in membrane applications as any soluble iron will cause rapid fouling. In water treatment there a number of commonly used forms which have slightly different properties and affinities for inhibiting precipitation of different scaling species. They typically have a molecular weight of 1,000–3,000 and common water treatment products are:

HEDP — 1-hydroxyethylidene 1-1-diphosphonic acid
AMP/ATMP — aminotri(methylenephosphonic acid)

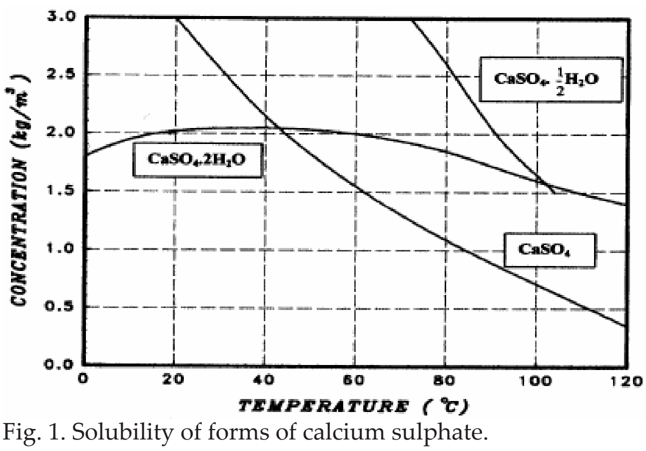

Fig. 1. Solubility of forms of calcium sulphate.

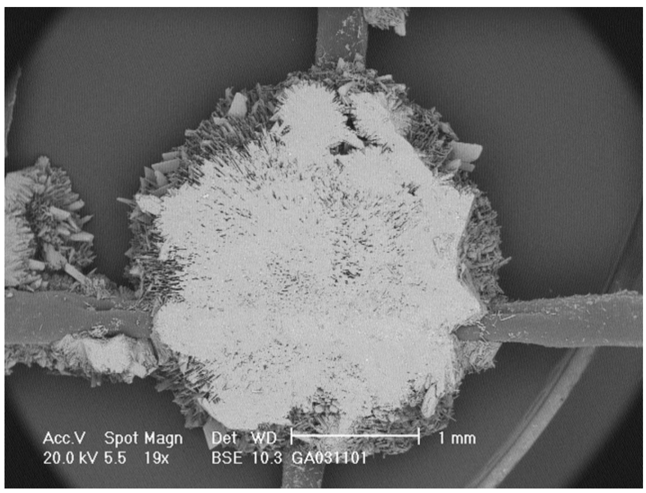

Fig. 2. Rosette formation on spacer.

PPCA — polyphosphinocarboxylic acid
PBTC — 2-phosphonbutane-1,2,4-tricarboxylic acid

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 2,000–10,000. Many of these polymers show some threshold effectivity whilst others have dispersion properties. Importantly they are ineffective at preventing iron deposition and instead tend to react with iron to produce iron acrylate which irreparably damages the membranes. The most commonly used products are:
PAA — polyacrylic acid
PMA — polymaleic acid
PCA — polycarboxylic acid
PAMAMS — polyaminoamide dendrimers
CMI — carboxymethylinulin

3.3. Crystal dispersion

Crystal dispersion occurs when the inhibitor chemisorbs onto the crystal surface and imparts an additional surface charge causing repulsion and ultimately dispersion. The growing crystal needs to be enveloped in a polymer of high molecular weight 20,000–40,000 to gain a significant surface charge. Few of the antiscalants on the market 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 are chosen to be combined into formulations and then tested against known standard performing antiscalants to see if an improved performance can be observed. Specific areas of interest for inhibiting calcium sulphate scale are summarised in Table 1.

Based on observations above certain assumptions regarding molecules that have differing properties can be made. Calcium sulphate on the other hand is strongly crystalline developing through weak needle and platelet forms to highly stable rosettes particularly in low flow areas around the membrane feed spacer [4]. These features of calcium sulphate scale formation were recognised when formulating the new antiscalant Genesys CAS. This product combines phosphonate threshold inhibitors polymeric compounds that distort crystals and have a dispersing effect.

Table 1
Properties of calcium sulphate scale

Species	Calcium sulphate
Crystal form	Monoclinic prisms, needle and platelets
Kinetics	Slow
Position	Last element
Seeding agents	Colloidal calcium sulphate

3.5. Inhibition mechanism

Threshold testing is conducted on formulations to establish a broad spectrum of activity and particular effectiveness against calcium sulphate. This was achieved by combining a blend of three different phosphonic and carboxylic acids. The phosphonate molecules prevent ordering and nucleation of calcium and sulphate ions preventing the crystallite from reaching critical mass for precipitation. The crystallite disintegrates releasing the phosphonate molecule to carry on its sub-stoichiometric reaction.

The phosphonate and polyacrylic molecules in the formulation are particularly effective at inhibiting calcium sulphate crystal formation as their anionic charge causes chemisorption on the particle surface inducing an overall negative charge resulting in particle repulsion and deformation of crystal structure and growth. It has been theorised by Darton [5] 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.

4. Calcium sulphate case study

Deep well extraction of groundwater can result in RO feed with a very high sulphate loading. A chemical manufacturing company 180 km east of Tehran Iran commissioned a 7,000 m^3/d two pass brackish water RO plant with brine recovery in September 2005. The system is a complex arrangement of 3 RO streams, each with pretreatment. (Fig. 3). The design consists of a first pass and second pass. The first pass comprises two identical skids with two stages of twenty and ten pressure vessels each with six membrane elements. Each skid RO1A and RO1B has a design permeate flow of 143 m^3/h at 63.5% recovery to give a total 1st pass production of 286 m^3/h. Hydranautics CPA 3 membranes are installed in both skids.

Pre-treatment for this pass consists of aluminium salt coagulant, hydrochloric acid injection, for lowering the feed pH and chlorination, ahead of multi-media filtration. A broad spectrum phosphonate based antiscalants Permatreat 191 was dosed after the multi-media filters

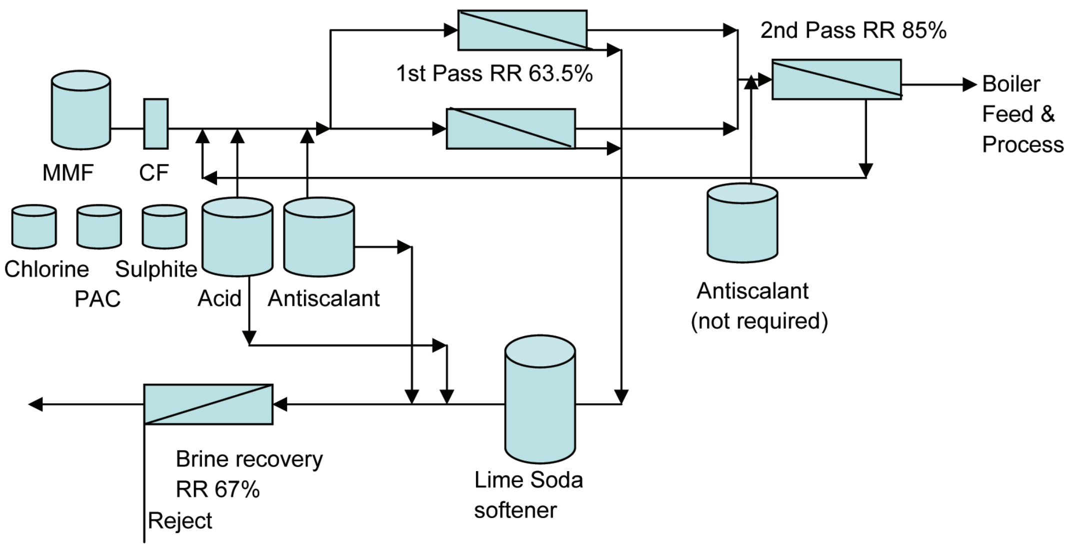

Fig. 3. Schematic of plant layout.

together with Sodium metabisulphite, (SMBS) which is added to de-chlorinate the feed prior the cartridge filters and high pressure pumping to the RO.

The 2nd pass RO2 is designed to operate at a recovery of 85% and is fitted with Hydranautics CPA4 membranes. The 2nd pass permeate is high quality water for boiler feedstock and process uses. The 2nd pass reject is returned back to the 1st. Pass feed at a point after the cartridge filters.

The 1st pass reject is sent for reprocessing through a brine recovery RO (BRRO). The theoretical conductivity of this water would be around 20,000 μScm^{-2} and has very high concentrations of scale forming elements. To permit 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. 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, designed to run at 67% recovery.

The raw water for supplying the plant is from underground wells. The full raw, feed and product water quality is shown in Table 2.

The chemical analysis from September 2007 showed a high calcium level of 785 mg/l, sulphate at 2,149 mg/l and bicarbonate of 141 mg/l. The pH was 7.5 and TDS 4,745 mg/l. An analysis using the Genesys Membrane Master software programme showed that calcium carbonate, calcium sulphate and barium sulphate all exceeded their solubility's respectively. The use of a conventional antiscalant could inhibit calcium carbonate and barium sulphate but not calcium sulphate.

The first pass trains A and B of the plant suffered from repeated calcium sulphate fouling which has resulted in a reduction of the recovery rates to 48% rather than the design specification of 63.5%. Even at low recovery rates the membranes were fouled after 4–5 weeks of operation with feed pressure increasing from 10 to 12.5 bar. The membranes were then replaced or cleans attempted. Cleaning was conducted when ΔP reaches 6.5 bar and when feed pressure reached 12.5 bar. Cleaning consists of exposing the membranes to a recirculating solution of ethylene diamine tetra acetic acid (EDTA) and sodium tripolyphosphate (STPP) at high pH. After flushing to remove the cleaning solution, there is 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 a rise in the feed pressure to 12.5 bar. There is therefore a residual fouling which is creating the ΔP and which is not being removed by this cleaning. However, flux did improve and so the cleaning had removed some foulant from the membrane surface but not from the feed/brine channel. Immediately after cleaning, 1st stage ΔP would be around 5.5 bar but this would rise in conjunction with the feed pressure until reaching around 6.5 bar after 4 weeks. The maximum operational ΔP, as recommended by the membrane manufacturer, would be 3.5 bar and the maximum excursion limit would be 4.1 bar. Beyond these limits, membrane damage can be expected. The membranes from the rear of the plant which could not be cleaned were all placed into RO1B which operated with a reduced permeated flow of 59 m^3/h. 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 dosage to oxidise iron and control microbiological growth required sodium meta-bisulphite neutralisation of the chlorine prior to the membranes. The subsequent

Table 2
Water analysis used for original plant design

Ion	Raw water		Feed water		Permeate		Concentrate	
	mg/l	meq/l	mg/l	meq/l	mg/l	meq/l	mg/l	meq/l
Ca	785.0	39.2	785.0	39.2	4.977	0.2	2142.0	106.8
Mg	153.0	12.6	153.0	12.6	0.97	0.1	417.5	34.4
Na	508.0	22.1	508.0	22.1	15.323	0.7	1365.1	59.4
K	12.0	0.3	12.0	0.3	0.451	0.0	32.1	0.8
NH_4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ba	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO_3	0.2	0.0	0.2	0.0	0.001	0.0	0.6	0.0
HCO_3	141.0	2.3	130.5	2.1	5.415	0.1	348.1	5.7
SO_4	2140.0	44.6	2148.9	44.8	12.56	0.3	5865.5	122.2
Cl	960.0	27.1	960.0	27.1	22.293	0.6	2591.4	73.1
F	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NO_3	10.0	0.2	10.0	0.2	1.643	0.0	24.5	0.4
B	0.0		0.0		0.0		0.0	
SiO_2	24.0		24.0		0.46		64.9	
TDS	4733.2		4731.6		64.1		12851.8	
pH	7.5		7.1		5.8		7.5	

acidic RO product water was dosed with caustic to raise the pH. The second pass is fed with permeate from the first pass operated at the design level of 85% without any problems because of the low level of scaling species in the feed water.

The brine recovery system had very 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.

4.1. Recommendations

The calcium sulphate specific antiscalant Genesys CAS dosage at 4.7 mg/l was introduced without acid dosing in November 2007 and has successfully prevented scale formation. Gradually the recovery rates have been increased to 61% and the membrane cleaning frequency has reduced from once per month to twice per year. The second pass permeate polisher is operating without the need for antiscalant at present. In addition to the first pass operating closer to the original design specification the brine recovery is now operable at 67% recovery. The acid dosage has been stopped as the calcium carbonate saturation index was not exceeded at a pH of 7.5 and additional acid had no effect on reducing calcium sulphate saturation point. With the acid removed there is an increase in permeate pH so caustic dosage is no longer required. The aluminium based coagulant has also been replaced with a polyamine based cationic flocculant which has reduced the SDI of the feed and helped the effectiveness of the lime soda softener. The well groundwater has a low level of microbiological activity so the chlorine dosage has also been removed along with the sodium metabisulphite chlorine neutraliser. By applying a dosage of 4.7mg/l of Genesys CAS to the feed the brine recovery system was recommissioned and now operates at a recovery of 60% and a feed flow of 131 m^3/h. This helps reducing the plants effluent discharge and produces permeate water with a TDS of 2000 mg/l which is used for non critical industrial processes.

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. Areas of savings are:

4.2.1. Water

The desired amount of product water can be created with less feed water by increasing the recovery rate. Table 3 shows that savings in precious ground water resource amount to over a million tons per year by increasing the recovery from 48% to 61%. Similarly the concentrate stream which would make up the effluent

Table 3
Feed water savings on 1st pass skid

	Permeate (m^3/h)	Feed @ 48% recovery (m^3/h)	Feed @ 61% recovery (m^3/h)	Feed saving (m^3/h)	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

discharge from the plant is also reduced significantly from 310 m^3/h to 182 m^3/h.

4.2.2. Energy costs

The water saving by increasing recovery can be translated into an electricity cost saving via reduced feed water pumping. Using the latest Hydranautics IMS Design RO Projection Programme the kWh/m^3 pump energy demand can be calculated for different operating conditions. In November 2003 the original design specification was for each skid to produce 143 m^3/h of product water operating at a recovery rate of 63.5%. In September 2007 Skid A produced 136 m^3/h of product water at recovery rate of 48%. The feed flow rate was 283 m^3/h which required 0.85 kWh/m^3 of pumping energy. In November 2007 the membranes were cleaned and the new sulphate specific antiscalant Genesys CAS was dosed at 4–5 mg/l. By February 2008 membrane scaling was being inhibited and recovery rates were gradually increased. As recovery rates increased the feed pressure increases to overcome the higher osmotic pressure. Recovery rates continued to increase throughout 2008 without calcium sulphate scale formation and the plant is now operating close to its design specification. The current pump energy use at 61% recovery rate is 0.62 kWh/m^3. This represents an annual energy saving of US$ 60,000 on this single skid assuming an electricity cost of $0.07/kWh (Table 4). This would be doubled if applied to each skid.

4.2.3. Acid dosing

Hydrochloric acid was dosed 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 of 35% hydrochloric acid per day. Calcium carbonate scaling can be easily inhibited with an antiscalant and reduced pH has no effect on inhibiting calcium sulphate scale therefore the dosage was removed saving 48 tons of acid per year at an estimated cost of $19,200.

4.2.4. Chlorine dosing

The original design called for chlorine dosing to reduce microbiological fouling. In order to retain a 0.2–0.5 mg/l residual of free chlorine a daily dose of 86 kg of 12.5% sodium hypochlorite was required. Sodium metabisulphite is dosed prior to the cartridge filter to neutralise any remaining chlorine to protect the membranes from oxidation damage. 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.

4.2.5. Membrane element replacement

Since commissioning in September 2005 it is reported that all of the membranes have been replaced over a two year period. This equates to 270 elements at an estimated cost of $162,000. Since November 2007 to February 2009

Table 4
Electricity cost savings

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, %	0.64	0.48	0.58	0.61
Feed flow, m^3/h	225.20	283.00	243.00	228.00
Permeate flow, m^3/h	143.00	136.00	140.00	139.00
Pumping energy, kWh/m^3	0.63	0.85	0.58	0.62
Energy, kWh	141.88	240.55	140.94	141.36
Total energy/annum, kWh	1225808.64	2078352.00	1217721.60	1221350.40
Pumping costs/annum	$85806.60	$145484.64	$85240.51	$85494.53

there have not been any membrane replacements. The membrane lifespan has been increased dramatically and schedule of replacement is now estimated at 70 membranes per year a potential annual saving of $39,000.

5. Conclusions

The development of speciality antiscalants for different scaling species allows stressed groundwater sources to be utilised economically. This is a vital factor when designing RO plant. The chemistry of the raw water is the major limiting factor and the antiscalant can have a huge impact on this. The case study above is a real example of the cost savings achieved by applying Genesys CAS a sulphate specific antiscalant. A summary of the annual savings is shown in Table 5.

This paper demonstrates that there are much more important parameters for antiscalant selection than the price/kg. The effects of operating the correct chemical programme include:

- Optimising the recovery rate and therefore minimising pumping costs
- Maintain membrane cleanliness extending the lifespan and reducing cleaning frequency
- Removing the dependency on dosing large quantities of non specific commodity chemicals

The use of groundwater as a source for RO plant will continue to expand as the world's resources diminish. One of the key limiting factors for RO design and operation is the source water quality. By combining various inhibitor molecules synergistic effects for different scaling species can be achieved. Once tested in the field and laboratory certain development products have become critical in ensuring economic and viable operation of RO plant with stressed brackish water feeds. Equating increased recovery rates to feed pump energy savings is now possible using new software from the membrane manufacturers. With this information the real costs associated with choosing the right antiscalant versus the cheapest can now be calculated.

Table 5
Case study cost savings

	Sulphate case study
Water saving, ton	1,121,280
Energy saving, kWh	857,002 (1 skid)
Energy costs saving, US$	60,000
Membrane replacement, US$	39,000
Chemical saving, US$	34,000
Total, US$	133,000

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