Desalination and Water Treatment
www.deswater.com

1944-3994 / 1944-3986
doi: 10.5004/dwt.2011.2364

31 (2011) 311–319
July

Successful antiscalant field trial — Optimization at higher pH and seawater temperature — Larnaca Desalination Plant

Filip Dutoy, Wiebo van der Wal*

thermPhos Belgium B.V.B.A Rue Laid Burniat, 3, B-1348 Louvain-La-Neuve – Belgium
Tel. +32 10481472; Fax +32 10481495; email: Wiebo.vander.wal@thermphosdequest.com

Received 14 July 2010; Accepted 8 April 2011

ABSTRACT

A desalination plant has been operating for a number of years at elevated pH both at the first and second reverse osmosis stages at feed seawater temperature up to 30°C. The main reason for operating at higher pH was to enhance the boron rejection capability of existing membranes and thus omit the operation of the second stage whenever lower seawater temperatures allow to do so and subsequently produce more water with less energy. However, a higher pH in conjunction with high seawater temperatures creates conditions for membrane scaling. Therefore an appropriate cost effective antiscalant has to be used at minimum dose level. This paper describes field trials of selecting and applying an appropriate antiscalant and the dosing optimisation process in function of feed seawater temperature and pH.

Keywords: Antiscalant; Chemicals; Scaling inhibition;, Magnesium hydroxide; Calcium carbonate; SWRO; Desalination; Reverse osmosis; Membrane

1. Introduction

Seawater desalination is a multi billion Euro business, estimated to be doubling its capacity world wide every 5 years. As the plants are increasing in numbers and scale, operational and maintenance costs are driven down resulting in prices below $0.5/m^3 of desalinated seawater.

Reduction of the costs of desalination of seawater is related to improvements in energy recovery systems, plant operation and plant systems, in membrane performance (in particular for boron removal), and in better pre- and post-treatment processes operation .

A more effective plant operation requires operating a desalination plant closer to its contractual criteria in order to save energy and resources i.e. operate the plant outside the traditional operating "box" and closer to its operational/contractual limits.

The desalination plant had to operate both the 1st and 2nd RO stages at higher pH in order to improve boron removal [1,2], because of the seawater temperature increase from 16°C to almost 30°C in the summer. The need for a well performing – cost effective antiscalant became now vital under these conditions. The cost of such chemical and the volumes required dictated that an appropriate antiscalant had to be selected and the dose rate had to be optimised.

This paper describes the methodology for choosing the proper antiscalant and optimizing the dose rate as a function of water pH and temperature in order (a) to minimise costs and at the same time (b) avoid membrane scaling.

* Corresponding author.

Presented at EuroMed 2010 — Desalination for Clean Water and Energy: Cooperation among Mediterranean Countries of Europe and MENA Region, 3–7 October 2010, David Intercontinental Hotel, Tel Aviv, Israel. Organized by the European Desalination Society.

2. The Larnaca Desalination Plant (Fig. 1)

The Larnaca Desalination Plant is described in other publications [3,4], and briefly described bellow [6].

The Larnaca Desalination Plant has been operating since 2001 with several innovative and leading design and operational systems, for example:

- First plant to operate with 8 membranes per pressure vessel
- First plant to have product outlet from both sides of the pressure vessel
- A most automated plant with enhanced monitoring of plant process systems

After plant commissioning an operational strategy in place [2] has led to improvements in plant performance and innovative modes of operation such as:

- Improve hydrodynamics and mixing processes in the pretreatment in order to reduce to the minimum chemical addition — flocculants
- Stop any acid addition in pre treatment and operated at normal seawater pH without affecting flocculation–coagulation process. This has a major added benefit of boron removal in the 1st RO stage.
- Introduce a complete system for assessing, cleaning and changing membranes — The Membrane Management System [5,6]
- Improve 1st stage performance so that the 2nd RO stage was not required to operate for half of the year
- Operate the 2nd stage at much higher pH to improve boron removal and meet the contractual requirements at high seawater temperatures
- A maintenance team who can also work as shift opera-

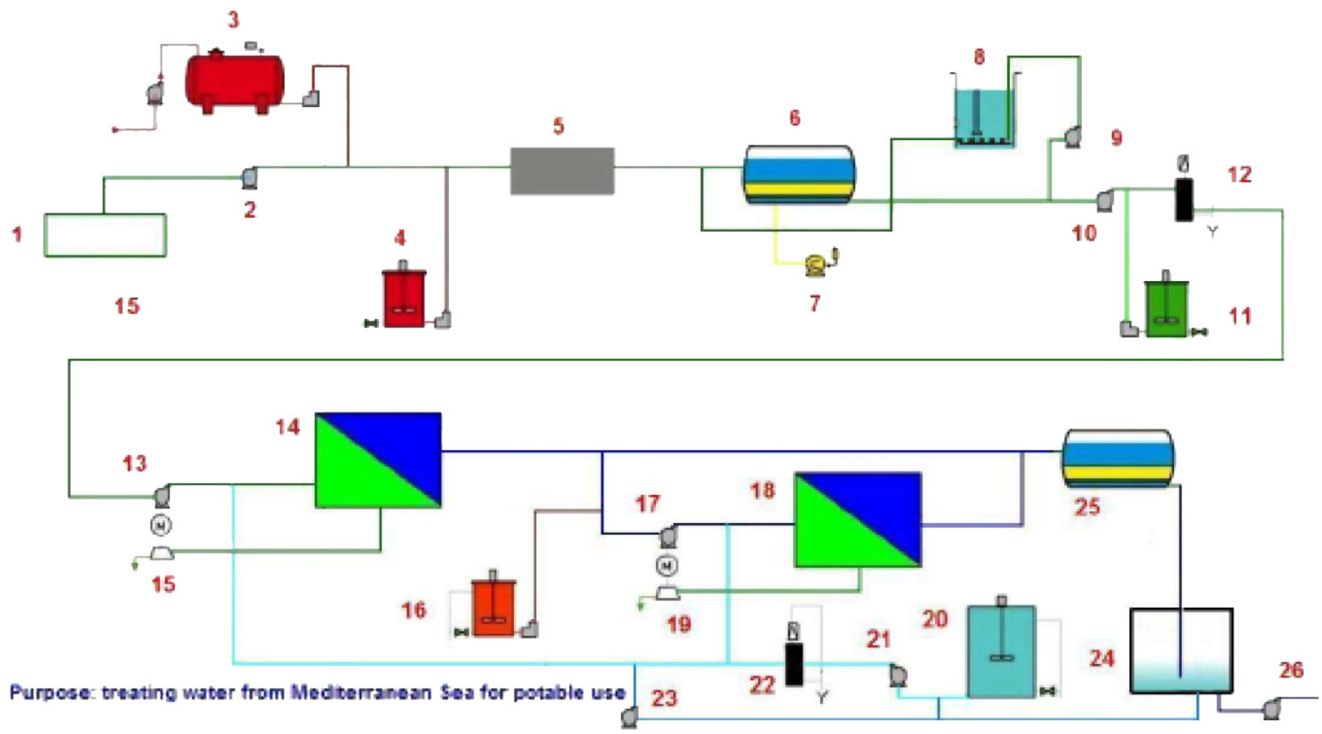

Fig. 1. Larnaca SWRO desalination plant. 1. Seawater intake; 2. Seawater pumps; 3. Sulfuric acid dosing system; 4. Coagulant dosing system, 5. Mixer room, 6. Open gravity sand filters, 7. Air blower, 8. Backwash tank for sand filters, 9. Booster pump for sand filters backwash tank, 10. Booster pumps, 11. Antiscalant dosing system for first pass, 12. Cartridge filters, 13. High-pressure pumps for trains in first pumps, 14. RO trains in first pass, 15. Energy recovery turbine first pass, 16. Antiscalant dosing system for second pass, 17. High-pressure pumps for trains in second pumps, 18. RO trains in second pass, 19. Energy recovery turbine second pass, 20. Chemical cleaning tank, 21. Chemical cleaning pump, 22. Cartridge filter (from chemical cleaning system), 23. Diesel pump for train flushing in case of energy power failure, 24. Permeate water tank, 25. Limestone gravel reactors, 26. Permeate pumps for distribution to the city.

Plant description: Plant location: Larnaca, Cyprus; Commissioning date: 2001; Nominal plant capacity: 54,000 m3/d; Recovert: 50% in first pass and 78% in second pass; Seawater pumps: 4; Filtration: open gravity sand filters (12 filters of two layers = 6 m/s filtration velocity; Cartridge filters: 12; Coagulation: through static mixer; Chemical dosing: previously sulphuric acid (not used actually), antiscalant in both passes and coagulant in first pass; Booster pumps: 4; Number of trains: 6 in first pass and 1 in second pass (this one with two stages); Number of PV's: 120 for first pass trains and 40:20 for train in second pass; Membrane number for PV: 8 in first pass and 8 in second pass; Membrane type: SWC3/SWC4 in first pass and ESPA 2 and ESPAB in second pass; High-pressure pumps: 6 in first pass (one per train) and 3 in second pass; Power recovery system: Pelton turbine; Chemical cleaning pump: 1; Permeate water tank capacity: 2,000 m^3.

tors and vice versa as part of their monthly normal working schedule

Other plant performance improvements were related to the optimization of pumping regimes and of the energy recovery system.

3. Boron removal, feed water pH and temperature

Seawater desalination plants all over the world have to produce drinking water which complies with EU or WHO regulations while at the same time achieving effective operation at lowest O&M cost. In particular the strict limit in boron of less than 0.5 ppm in parts of the world, has enhanced the energy requirements substantially. This desalination plant has been operating since 2001 with a contractual commitment to produce water with boron less than 1.0 ppm.

However, in the seawater desalination field, this is not an easy to meet criterion since the boron concentration in seawater (especially in the Mediterranean) is comparatively high (over 5.0 ppm). Options available to solve the boron issue are both costly with high energy requirements.

The boron rejection in RO membranes, depends on salinity, temperature, pH, membrane elements properties, system design and operational parameters e.g. average permeate flux, recovery etc [1]. The difficulty of removal of boron is mainly linked to the fact that at lower seawater pH (e.g. pH = 7.0 which is an optimum pH for flocculation purposes) the majority of boron exists as uncharged boric acid with a small fraction as negatively charge as shown below. However, the fraction of negatively charged borate ions increases as seawater pH increases. The borate ion becomes a dominant species as pH increases beyond the pKa (9.14 at 25°C) as dictated by the equilibrium Eq. (1) and shown in Fig. 2.

$$H_3BO_3 \Leftrightarrow H_3BO_2^- + H^+ \quad pK_a = 9.14 \tag{1}$$

The surfaces of SWRO membranes are negatively charged. Consequently, as the pH increases, the charge repulsion between the negatively charged borate ions produced and the negatively charged membrane surfaces effectively decrease diffusive transport of boron through the membrane. Boron removal is thus largely dependent on pH as established in the literature and other studies. Boron removal at pH = 8 is between 75–90% [3], depending on water temperature.

In general a plant is originally designed to operate at lower pH (around 7) for optimum coagulation/flocculation with the use of ferric salts technology. The optimum coagulation pH has to do with the iso-electric point from the colloids and the necessary pH to achieve coagulation. In order to obtain best flocculation ,the appropriate pH is at the point where the hydroxide ions achieve the minimum in solubility. This pH and the minimum solubility

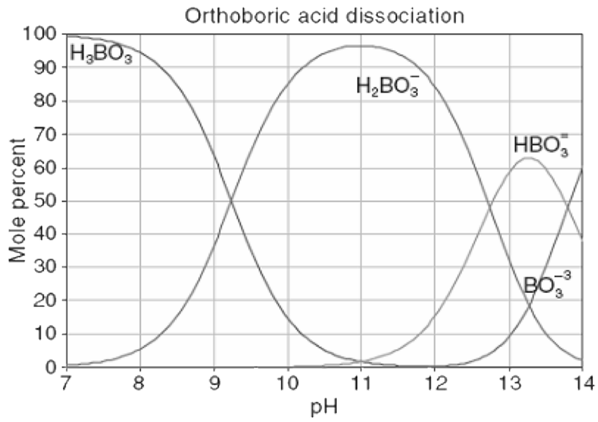

Fig. 2. Dissociation of orthoboric acid into more ionic forms [1].

are strongly depending of the ionic strength and of the presence of organics (humic acids) [7]. However the lowered seawater pH reduces the boron removal capability of the 1st stage RO membrane process. Consequently now it will need the operation of a 2nd RO stage to maintain boron below the required levels and this will result in a higher energy consumption

Thus an optimum pH is required to satisfy both the pre-treatment/flocculation process as well as the reverse osmosis membrane boron removal process. Extensive work has been carried out at desalination plants for the last few years where pre treatment processes have been optimized to achieve good flocculation results at the natural seawater pH of 8.2 [3,5,6].

The use of higher pH seawater substantially enhances boron removal, particularly in the case of 1st RO stage where most of the membrane area is placed and 80% of the seawater is purified. Thus small increases in pH can improve boron removal favourably.

However by increasing the pH (particularly at high seawater temperatures) it also increases the membrane scaling risk of the 1st stage. The potential scaling depends on the plant operational conditions for the specific RO stage, seawater composition ,pH, temperature, alkalinity, calcium content, TDS.

The effect of seawater temperature on boron removal is documented in the literature [3] although more research work will help plant operators to optimise their plant. For high salinity seawater with high boron content in hot climates, (the Mediterranean Sea above 25°C) boron removal decreases with increasing seawater temperatures at an exponential rate. Therefore for a given seawater pH, the potential of scaling can increase substantially if appropriate scaling preventive measures are not in place.

4. Scale formation in RO membrane stages

When scaling occurs two main types of scaling have been observed (a) calcium carbonate and (b) magnesium

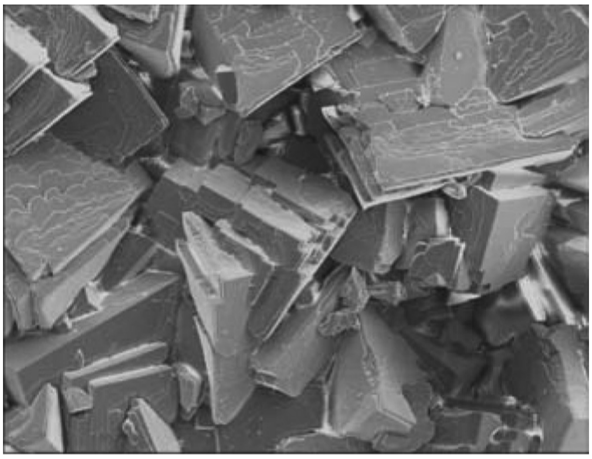

Fig. 3. Calcium carbonate crystals — SEM picture (courtesy of thermPhos).

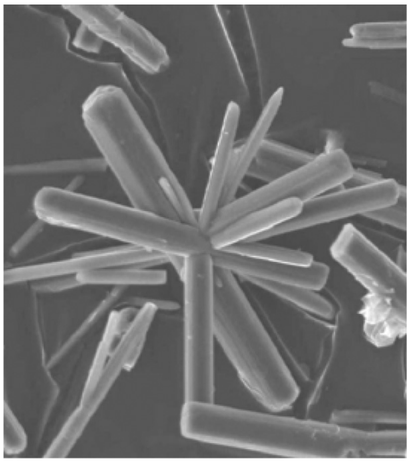

Fig. 4. Needle type — brucite crystal SEM picture (courtesy of thermPhos).

hydroxide scaling. These are not the only ones since other substances can form the basis of scaling. However these two are the most common.

Calcium carbonate scaling takes place in the form of flaky crystals — shown in the electronic microscope photo in Fig. 3.

Such scaling, once developed and settled, particularly at the rear membranes of a pressure vessel, will attach itself to the membranes surface area and cannot be removed even with an aggressive chemical cleaning of the membranes. Membrane scaling will eventually manifest itself as an increase in the pressure drop across pressure vessels and whole RO stages/trains. At higher seawater feed pH (above pH = 9.0) a more common scaling is caused by residual magnesium, not being removed in the first seawater RO stage. This could precipitate as magnesium hydroxide ($Mg(OH)_2$) in the second RO stage. This scale, called brucite, has a very low solubility in water and forms needle type crystals as shown in the electron microscopy photo (Fig. 4).

Separate investigations where carried out on the 1st and 2nd stage RO membrane processes to study the potential of scaling under the operating conditions.

Potential scaling for both 1st and 2nd RO stages consists of calcium carbonate scaling. For the 2nd stage due to the higher pH, magnesium hydroxide ($Mg(OH)_2$) scaling has to be taken into account. Thus, more emphasis was put on magnesium based scaling for the 2nd RO stage process due to the higher operational pH. A laboratory simulation of the $Mg(OH)_2$ saturation was made under typical second stage conditions as shown in Fig. 5.

Results obtained from the graph above provide the maximum solubility of $Mg(OH)_2$ vs. pH at a temperature of 30°C. The rapid solubility decrease with an increasing pH can be observed.

The two scaling species described above are crystalline and in order to avoid their formation, appropriate

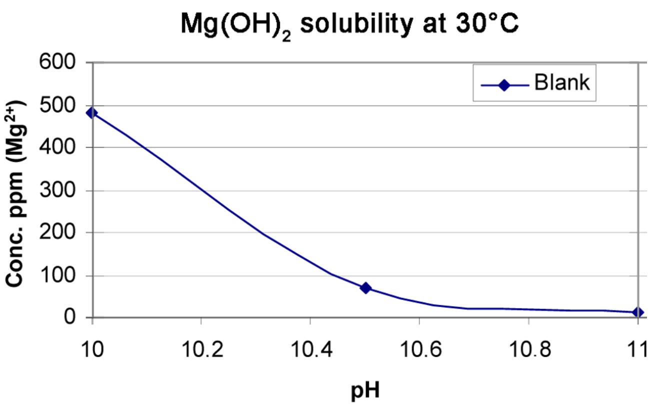

Fig. 5. $Mg(OH)_2$ solubility vs. pH at seawater temperature of 30°C.

antiscalants must have a specific mechanism to inhibit the crystalline form or their precursors. ThermPhos ,with the help of research work carried out ,went through a selection process for the most appropriate antiscalant (phosphonate based) and its optimum dosing rate.

5. How does an antiscalant work?

ThermPhos has developed a process for selecting appropriate antiscalants according to specific requirements. The antiscalants are based on phosphonate technology and act simultaneously as crystal growth modifier, sequestering agent for metals ions and dispersing agent. The sum of the above mentioned properties results in a "threshold scale" inhibitor.

The "threshold effect" (Fig. 6) is the prevention of precipitation from supersaturated solutions at substoechiometric amounts of inhibitor. This phosphonate based technology is able to increase the induction time and simultaneously decrease crystal seeds growth.

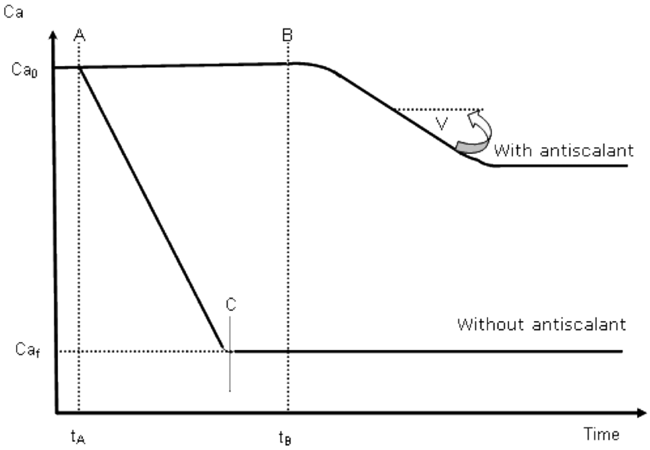

Fig. 6. Threshold effect of organophosphonate on calcium carbonate precipitation. AB: induction time; V: growing rate; AC precipitation phase; Ca = calcium concentration.

ThermPhos developed a wide range of phosphonate based molecules from which phosphonate based antiscalants are produced. Although the generic antiscalant is very effective in a wide variety of precipitating systems, more tests are carried out for specific cases. Also in the case of this paper, final adjustments of the composition of the product have resulted in a specific antiscalant.

6. Choosing the correct antiscalant

The Larnaca Desalination Plant (LDP) was originally designed to operate at a lowered seawater feed pH at around 7. This pH is needed for an optimal flocculation process, with the use of a ferric salt solution, dosed before the pre treatment sand/anthracite filters [1] — section 2.

However the lowered seawater pH reduced the boron removal capability of the first stage RO membrane process and resulted initially in the use of the second stage RO process all the year round [4]and a higher energy consumption. LDP as part of its plant operation optimization strategy [2] has lead the way in operating for a number of years now at normal seawater feed pH (pH 8.2) by suppressing the acid injection (originally used to lower the pH to the value of 7 used original as optimum flocculation conditions). The higher pH has improved the overall boron rejection capability of the 1st stage RO membranes, where for more than 6 months of the year the 1st stage RO process produced product waster at less than 1.0 ppm boron (thus the 2nd RO stage was not necessary).

LDP has been monitoring very carefully the seasonal seawater conditions, e.g. chemical/biochemical constituents based on the seawater temperature patterns as shown in Fig. 7.

Based on the seawater temperatures the mode of plant operation was divided in three different periods:

Period 1: 16–20°C
Period 2: 21–25°C
Period 3: 26–30°C

The Larnaca Desalination Plant has been investigating with Thermphos the selection of the appropriate antiscalant and its optimum dose rate in function of seawater temperature range periods shown above. Each period was defined by a different mode of operation where various plant operational parameters had different values, e.g. flocculant dosing, SDIs, RO process feed pressures, ΔPs,

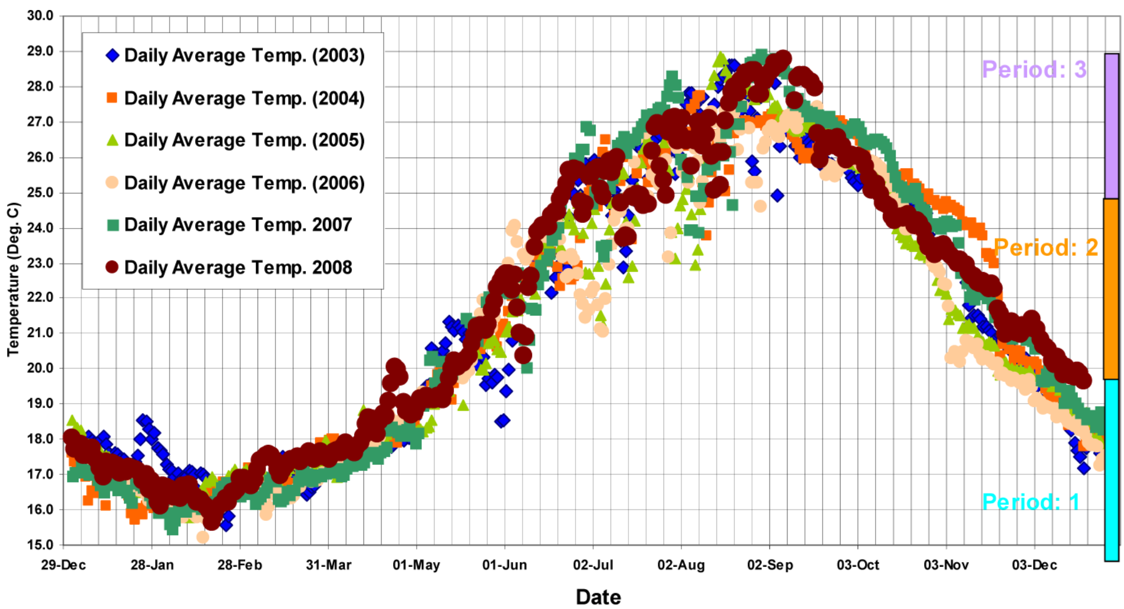

Fig. 7. Seawater temperature variations — basis of antiscalant dosing.

recoveries, water quantity and quality, 2nd RO stage operation etc.

6.1. First RO stage antiscalant considerations

As a first step for investigating potential scaling species, seawater analyses were made at different times. Typical results are shown in Table 1. Following parameters were taken into consideration:

- seasonal temperature variability (from 15°C to 30°C)
- seawater composition
- pH and operational conditions

Membrane autopsies of rear membranes with visual and other tests where also helpful to assess potential scaling.

In order to determine the parameters where scaling could occur, saturations indices such as S&DSI where calculated [8] for the highest scaling potential i.e. the rear membrane element (in a pressure vessel of 8 membranes) ,taking into account the specific operational conditions for that specific RO stage. For the seawater composition we refer to Table 1. pH, temperature, alkalinity, calcium content, TDS, etc, were taken into account. The results of the investigation by LDP are shown in Fig. 8 where S&SDI is shown as a function of seawater temperature and pH.

As a general rule of thumb an antiscalant is required whenever the S&DSI is higher than 0.5. At natural seawater pH of 8.2 and for a seawater temperature variation of 15–30°C, the untreated S&DSI values for the 1st RO stage vary between 0.9 and 1.3 (see blue bar graph above). Hence an antiscalant is required for the 1st stage all year round.

Based on saturation index calculations, operational parameters of LDP and potential scaling, thermPhos selected a phosphonate based antiscalant named SPE0111. This antiscalant was able to increase the solubility of calcium carbonate to the level of an S&DSI of 2.6. This saturation limit is sufficient to operate the 1st stage RO process of LDP in a safe mode regarding calcium carbonate scaling potential. SPE0111 is classified as non-hazardous and is complying with EU Standard 60 regulation for drinking water plants. The dose rate for the initial trial period under the most severe conditions (pH, temperature) was determined and a trial was conducted while monitoring the RO 1st stage process. The trial was initiated in March 2007 and successfully completed 12 months later.

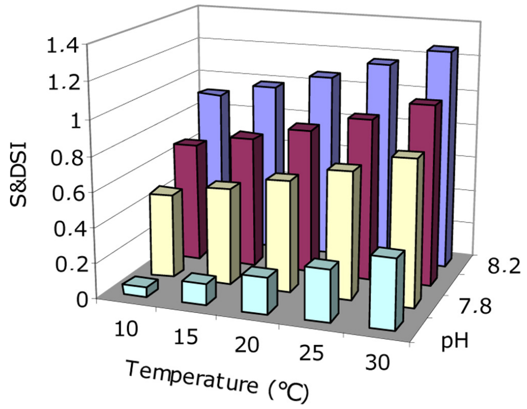

Fig. 8. Calculated S&DSI values of LDP (1st RO stage) vs. pH and seawater temperature.

Table 1
Typical LDP seawater feed analysis

Parameter	Values used for simulations
pH	8.2
Conductivity, μS/cm	52,000
TDS, mg/l	39,000
Chlorides, mg/l Cl^-	22,410
Sulphates, mg/l SO_4^{2-}	3,400
Bicarbonate, mg/l HCO_3^-	128
Fluoride, mg/l F^-	2
Sodium, mg/l Na^+	11,670
Potassium, mg/l K^+	308
Calcium, mg/l Ca^{2+}	599
Magnesium, mg/l Mg^{2+}	1,453
Boron, mg/l B	5
Iron, mg/l Fe	<0.05
Silica, mg/l SiO_2	0.4

6.2. Second RO stage antiscalant considerations

The performance of the optimised 1st RO stage was such that the operation of the 2nd RO stage was not required for more than 6 months of the year while meeting all contractual water quality and quantity criteria [3]. The work leading to this result was carried out over several years and has been described in previous publications [2,5,6].

During the warmer months of the year however, the 2nd RO stage had to operate in order to maintain the water quality requirements of boron. The permeate from the first pass is split into low salinity permeate from the front of the vessel and high salinity permeate from the back of the vessel [5]. The high salinity permeate was then sent to the second RO stage. Before entrance into the second stage the pH was increased by addition of caustic soda.

As part of antiscalant optimization and overall plant operation strategy the possibility of using the same antiscalant — SPE0111 for the 2nd RO stage was investigated.

The product SPE0111 had now to specifically address the issue of brucite scaling. Laboratory tests were carried out in order to determine optimum antiscalant dosage to cover both the water temperature and pH operating ranges of the 2nd stage. The effect of the SPE0111 antiscalant on the solubility of brucite is shown in Fig. 9.

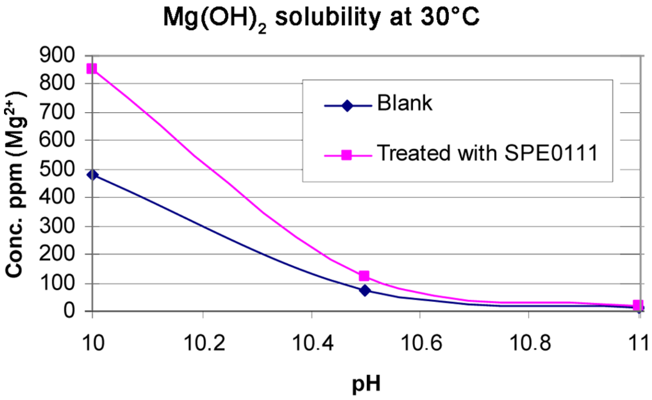

Fig. 9. Effect of SPE0111 on the solubility of brucite.

As Fig. 9 indicates SPE0111 is able to control brucite precipitation by increasing the solubility approximately two fold in the typical conditions of he second stage (i.e. pH range of 9.2–10.2 and a recovery of 80%). As a first indication it was decided to trial the SPE0111 at optimum dosing during the operation of the 2nd stage in the warmer months of the year. The results were successful meaning no scaling was observed nor was there an increased pressure drop over the 2nd stage during its operation. However, this trial has to be repeated specially at the highest seawater temperatures (above 28°C) and pH to establish confidence.

7. 1st stage RO field trial — applying/optimising antiscalant dose

The field trial was done for a whole year in order to assess the antiscalant performance taking into consideration seasonal variations.

7.1. Analytical method for SPE0111 determination

In order to validate the antiscalant dosage, an accurate spectro-photometric analytical method was used to analyze the level of antiscalant in the feed and brine streams of the RO stage for each of the six trains of LDP. Table 2 provides an example of field analytical results collected during the trial period on selected trains.

The ratio of brine and feed analytical values was monitored for each train and this was done by checking for any "loss" of antiscalant as a sign of potential scaling. The average value of the ratio over the trial period, was between 95–105%. With this results and taking into account the fluctuations in operational parameters and accuracy of analytical method it was concluded that the correct dosage of antiscalant was taking place and no scaling occurred. However for cost effectiveness the dosing of the antiscalant requires optimisation in function of seasonal and plant operational variations.

7.2. Antiscalant performance monitoring

During the field trial the systems performance was monitored using data from the on-line SCADA system where parameters such as ΔP feed/brine, production rate, permeate quality, recovery, water quality etc were recorded. Also normalised values were calculated to support the 1st RO stage performance. However a quick and simple monitoring of the performance of the antiscalant was based on the measurement of the pressure difference of the trains at different times of the year, while taking into consideration key factors such as the seawater temperature, membrane changes in trains etc.

In Fig. 10 a comparison of ΔP of the six trains is made after 12 months of the field trial.

Table 2
Antiscalant analytical results using spectrophotometric method

	SPE 0111(ppm)		SPE 0111(ppm)	
	Start of trial		Results of later date	
	Analyzed	Calculated	Analyzed	Calculated
Train A				
Brine	2.72	2.36	2.66	2.35
Feed	1.55	1.26	1.37	1.26
Recovery (%)	46.60%		46.40%	
Train C				
Brine	2.41	2.33	2.59	2.32
Feed	1.30	1.26	1.40	1.26
Recovery (%)	46.00%		45.70%	
Train E				
Brine	2.59	2.39	2.66	2.39
Feed	1.44	1.26	1.40	1.26
Recovery (%)	47.30%		47.30%	

Fig. 10. ΔP of all trains during the same period of time for different years.

The results show that despite that after one year of operation while using the SPE0111 antiscalant, there is no increase in the pressure difference of the Trains, where normally after one year of operation ΔP should show some increase. This indicates that the SPE0111 antiscalant is functioning satisfactorily. However, during the year of the field trial it is a fact that both (a) membrane changes were made on the trains as well as (b) chemical cleaning on the membranes. This assists to minimise increases of ΔP of the trains. The conclusion is that the antiscalant, in conjunction with the membrane changes and cleaning, is functioning well to avoid scaling of the membranes at the high seawater temperatures and elevated pH.

7.3. Dosing optimisation of antiscalant

In December 2008 the Larnaca Desalination Plant has completed its 2nd plant expansion, increasing its production by 20%. Thus the need for optimization of antiscalant has become even more important.

As mentioned above the feed water temperature is one of the key factors affecting the potential for scaling.

The seawater temperature profile was divided into three periods of modes of plant operation as described in section 6. For each mode of operation an optimum dose rate was recommended as shown in Fig. 11.

The dosage of the antiscalant was based on the methodology described above. The actual dosing optimisation at different seawater feed temperatures is yet to be completed. However, this paper clearly describes that with good plant monitoring and careful assessment, antiscalant dosing can be varied as a function of seawater temperature and pH — seasonal mode of operation of the plant which can result in cost effective application of antiscalant.

8. Conclusions

The Larnaca Desalination Plant 1st and 2nd RO stages are operated at a range of seawater feed temperatures from 16 to 30°C and increased seawater pH. The need for the use of cost effective, well performing antiscalant was here essential.

In co operation with thermPhos a methodology was implemented to select appropriate antiscalant, as well as to optimise the dosing in function of seawater temperature and pH. This minimised the potential for scaling of both 1st and 2nd RO stages at elevated pH values. The objective for improving boron removal of the membranes was achieved, enhancing the overall plant performance.

The thermPhos antiscalant SPE0111 has proven to cope with the plant's seasonal and operational variations and in conjunction with the implemented membrane changes and chemical cleaning, no scaling was recorded on the membranes.

An optimization of the antiscalant dosing as function of seawater temperature and pH was recommended.

Acknowledgement

Herewith we would like to thank IDE technologies for their input and support in order to accomplish the results as mentioned in this paper.

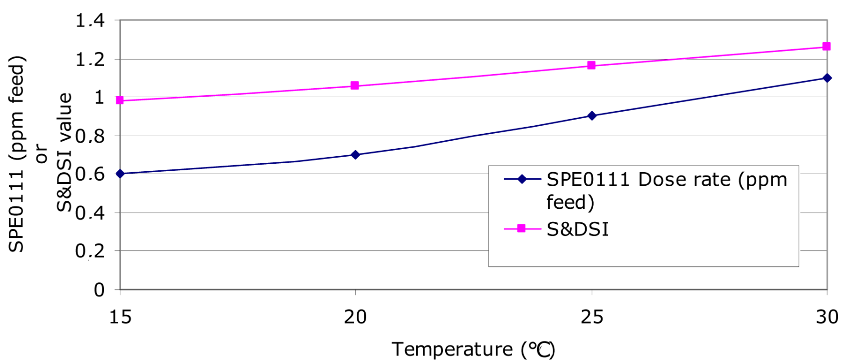

Fig. 11. Dose rate of SPE011 in the feed vs. mode of operation and S&DSI.

References

[1] M. Faigon and D. Hefer, Boron rejection in SWRO at high pH conditions vs. cascade design, Desalination, 223 (2008) 10–16.

[2] E. Koutsakos and D. Moxey, Larnaca desalination plant, Cyprus — from an efficient to an effective plant operation, Desalination, 221 (2008) 84–91.

[3] E. Koutsakos and D. Moxey, More water less energy and reduced CO_2 emissions – The Larnaca Desalination Plant, Desal. Wat. Treat., 5 (2009) 68–73.

[4] E. Koutsakos and K. Savvides, Larnaca Desalination Plant operation — A client contractor perspective, Desalination, 184 (2005) 157–164.

[5] C. Bartels, S. Cioffi, S. Rybar, M. Wilf and E. Koutsakos, Long term experience with membrane performance at the Larnaca Desalination Plant, Desalination, 221 (2008) 92–100.

[6] E. Koutsakos and D. Moxey, Membrane management system, Desalination, 203 (2007) 307–311.

[7] Memento Techniques de l'Eau, 10ème ed., Degrémont, ISBN 2-7430-0717-6, p. 218.

[8] Standard Practice for Calculation and adjustment of the Stiff & Davis stability index for reverse osmosis - ASTM D 4582-91 (Reapproved 2001).