Successful antiscalant field trial - Optimization at higher pH and Sea water Temperature – Larnaca Desalination Plant

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Abstract

Larnaca Desalination Plant has lead the way in operating for a number of years at elevated pH both at the first and second Reverse Osmosis stages at higher feed sea water temperature up to 30°C. The main reason for the higher pH was to enhance the boron rejection capability of existing membranes and thus reduce the need for a second stage at lower sea water temperatures and subsequently produce more water at less energy. However, higher pH in conjunction with high sea water temperatures create conditions for membrane scaling. Therefore an appropriate cost effective antiscalant has to be used with minimum dosing rate. This paper describes field trials of choosing and applying an appropriate antiscalant and dosing optimisation as a function of feed sea water temperature and pH.

1.0 Introduction

Sea Water 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 in scale the operational and maintenance costs are driven down with sea water desalinated prices below $0.5 per cubic meter.

Reduction of the costs of Desalination of seawater is related to improvements such as improved energy recovery systems, more efficient plant operation and systems, advancements in membrane performance (in particular for boron removal), better pre and post treatment processes operation etc.

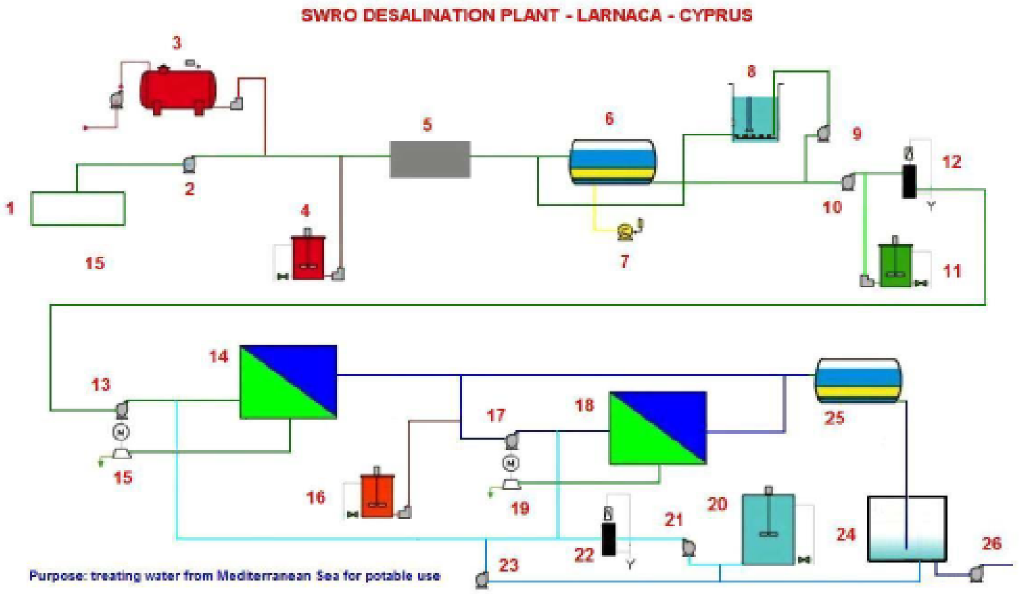
A more effective plant operation requires to operate a desalination plant closer to its contractual criteria in order to save energy and resources i.e. operate the plant outside the traditional operating "box" and closer to its operational / contractual limits.

For example the Larnaca Desalination Plant, operated both the 1st and 2nd RO stages at higher pH as the sea water temperatures increase from 16°C to almost 30°C in the summer, to improve boron removal (1,2). The need for well performing – cost effective antiscalant became vital. The cost of such chemical and the volumes required dictated that an appropriate antiscalant had to be chosen as well as optimise its dosing.

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

2.0 The Larnaca Desalination Plant

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



LEGEND
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 pass
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 pass
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 m^3/day
Recovery: 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 sulfuric 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 2 stages)
Number of PV's: 120 for first pass trains and 40:20 for train in second pass
Membranes number per 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

The Larnaca Desalination Plant has been operating since 2001 with several innovative and leading designs 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 in improving the plant performance and innovative modes of operation such as:

- Improve hydrodynamics and mixing processes in the pre treatment in order to reduce to the minimum chemical addition – flocculants
- Stop any acid addition in pre treatment and operate at normal sea water 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 sea water temperatures
- A maintenance team who can also work as shift operators and vice – versa as part of their monthly normal working schedule

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

3.0 Boron removal and feed water pH and temperature

Sea Water 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. The Larnaca Desalination Plant (LDP) 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 criterion to meet since the boron concentration in seawater (especially in 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, seawater & pH, membrane elements properties, system design and operational parameters e.g. average permeate flux, recovery etc (1). The difficulty in removing boron is mainly linked to the fact that at lower seawater pH (e.g. pH = 7.0 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 sea water pH increases. The borate ion becomes a dominant species as pH increases beyond the pKa (9.14 @25°c) as dictated by the equilibrium Eq. 1 and shown in Figure 1, below.

$$H_3BO_3 \Leftrightarrow H_3BO_2^- + H^+ \quad \mathrm{pK_a} = 9.14 \qquad \text{..............................}\textbf{Eq. 1}$$

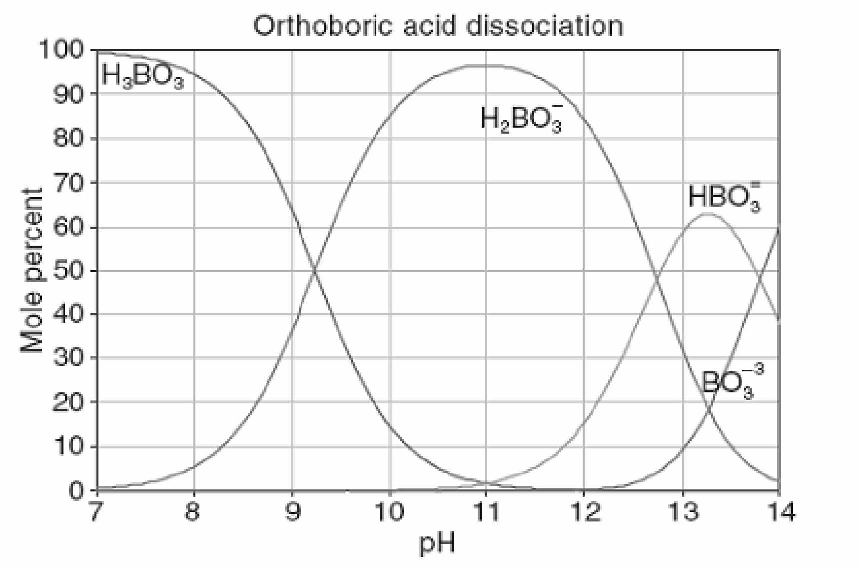


Figure 1: Dissociation of orthoboric acid into more ionic forms (1)

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 e.g. Boron removal at pH 8 is between 75% to 90% (3), depending on water temperature.

In general per treatment processes are designed to operate at lower water pH, around 7, for optimum coagulation/flocculation using 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 an appropriate pH is at the point where the hydroxide ions achieve the minimum in solubility. This pH and the minimum solubility are strongly depending of the ionic strength and of the presence of organics (humic acids) (7). However the lowered sea water pH reduces the boron removal capability of the 1st stage RO membrane process and consequently results in high energy consumption since it needs the operation of 2nd R.O. stage to maintain boron below the required levels.

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 Larnaca Desalination Plant (LDP) for the last few years where pre treatment processes have been optimized to achieve good flocculation results at natural sea water pH of 8.2 (3,5,6)

Operating at higher pH sea water, substantially enhances boron removal, particularly in the case of 1st RO stage where most of the membrane area is placed and for LDP 80% of the sea water is treated, thus small increases in pH can improve boron removal favourably.

However by increasing the pH (particularly at high sea water 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 (ions) and pH, temperature, alkalinity, calcium content, TDS etc.

The effect of sea water temperature on boron removal is documented in the literature (3) although more research work into the issue will help plant operators to optimise R.O processes better. For high salinity seawater with high boron content in hot climates, e.g. Mediterranean Sea - Cyprus especially above 25°C, boron removal decreases with increasing sea water temperatures at an exponential rate. Therefore for a given sea water pH, the potential of scaling can increase substantially and quickly if appropriate scaling preventive measures are not in place.

4.0 Scaling formation in R.O membrane stages

When scaling conditions develop two main types of scaling have been observed (a) Calcium Carbonate and (b) Magnesium 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 the form of flake crystals – shown in the electronic Microscope photo below in Figure 2

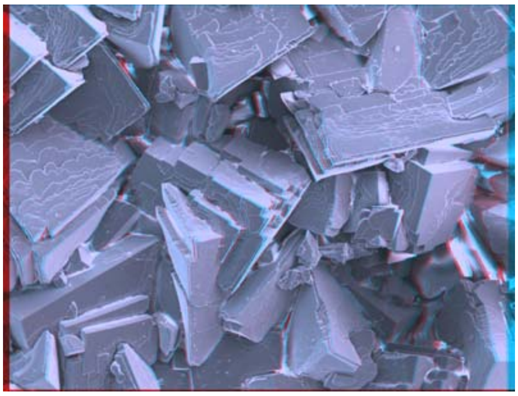


Figure 2: Calcium carbonate crystals - SEM picture (courtesy of ThermPhos)

Such scaling once developed and settled, particularly at the rear membranes of a Pressure Vessel, it will attach itself to the membranes surface area and not removed even with the most aggressive chemical cleaning of the membranes. Membrane scaling will eventually manifest itself as an increase in the pressure drop across pressure vessels and whole R.O. stages / trains. At higher sea water feed pH (above pH = 9.0) a more common scaling is caused in the 2nd RO stage by residual magnesium, not being removed in the first sea water R.O. stage. This could precipitate as magnesium hydroxide ($Mg(OH)_2$) in the second R.O. stage. This scaling species, called brucite, has a very low solubility in water and forms needle type crystals as shown in Figure: 3 below.

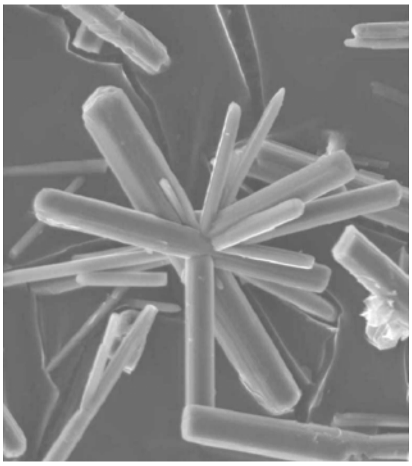


Figure 3: Needle type - Brucite crystal SEM photo (courtesy of ThermPhos)

Separate investigations where carried out or the 1st and 2nd stage R.O. membrane processes to study the potential of scaling under the LDP's operating conditions.
At LDP, potential scaling for both 1st and 2nd R.O. stages is calcium carbonate. For the 2nd stage due to the higher pH, Magnesium Hydroxide ($Mg(OH)_2$) scaling has to be taken into account more seriously. Thus, more emphasis was put on Magnesium based scaling for the 2nd R.O. stage process due to the higher pH being operated. A laboratory simulation of the $Mg(OH)_2$ saturation index was made under typical second stage condition as shown below.

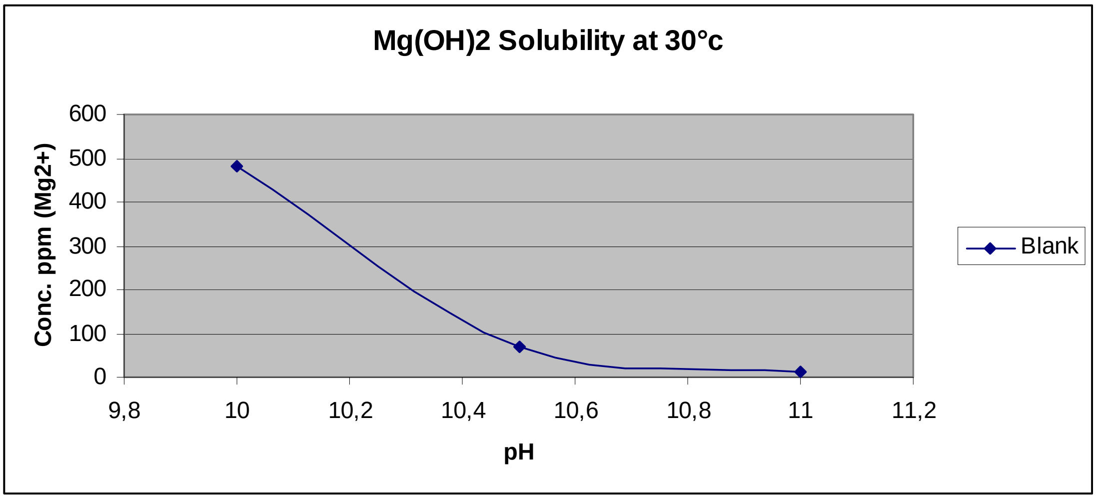


Figure 4: Mg(OH)2 solubility versus pH at sea water temperature of 30°c

Results obtained such as the graph above provides the maximum solubility of $Mg(OH)_2$ versus pH at a given temperature. The rapid solubility decrease with an increasing pH was noted.

The two scaling species described above are crystalline and in order to avoid their formation, appropriate antiscalants must have a specific mechanism to inhibit the crystalline form or their precursors. ThermPhos in cooperation with research work carried out at Larnaca Desalination Plant used a selection process for the most appropriate antiscalant (phosphonate based) and its optimum dosing.

5.0 How Antiscalant works

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

The "threshold effect" (Figure 5) is the prevention of precipitation from supersaturated solutions at sub-stoechiometric amounts of inhibitor. This phosphonate based technology is able to increase the induction time and simultaneously decrease crystal seeds growth.

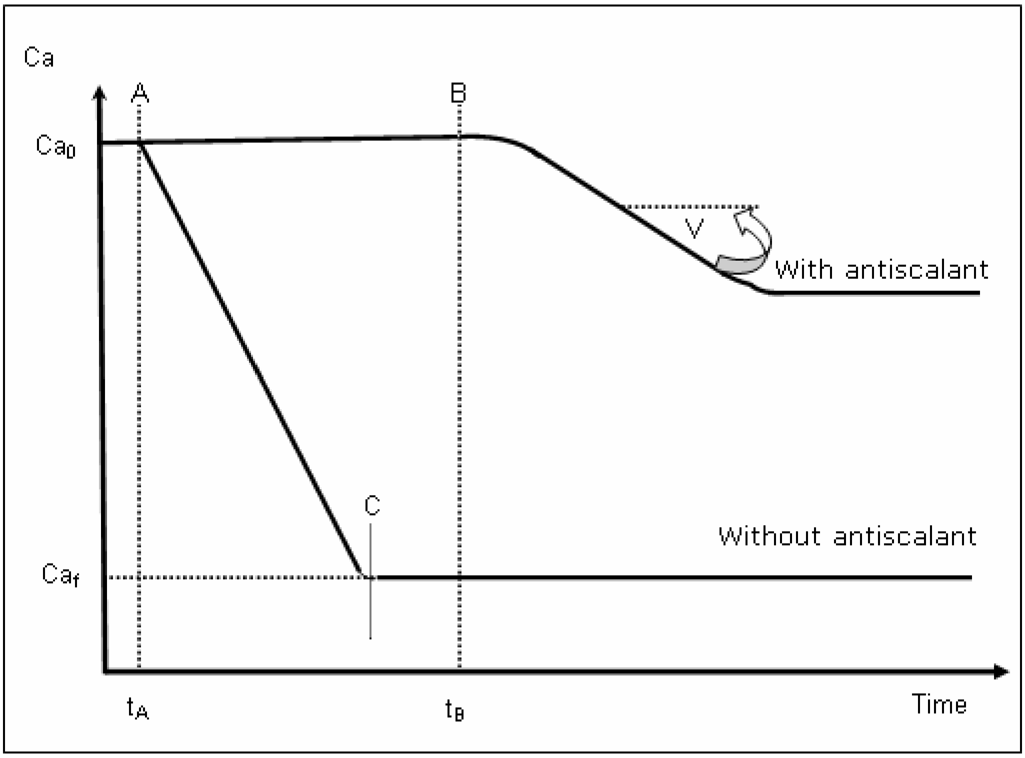


Figure 5: Threshold effect of organophosphonate on calcium carbonate precipitation (7)

Legend or Figure 5:

- AB: induction time
- V: growing rate
- AC, BF 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 for final adjustment of the composition of the final product has resulted in a specific antiscalant.

6.0 Choosing the correct antiscalant

The Larnaca Desalination Plant was originally designed to operate at lower sea water feed pH at around 7 for optimum flocculation process which uses Ferric salt solution dosed before the pre treatment sand / anthracite filters (1). However the lowered seawater pH reduced the boron removal capability of the first stage RO membrane process and consequently resulted initially in higher energy consumption using the second stage R.O. process all the year round (4). LDP as a first step and part of its plant operation optimization strategy (2) has lead the way in operating for a number of years now at normal sea water feed pH (pH 8.2) by suppressing the acid injection (used to lower the pH to the value of 7, as optimum flocculation conditions). The higher pH has improved the overall boron rejection capability of the 1st stage R.O. membranes, where for more than 6 months of the year the 1st stage R.O. process produced product waster at less than 1.0 ppm (thus the 2nd R.O. stage was not necessary).

LDP has been monitoring very carefully the seasonal sea water conditions e.g. chemical / biochemical constituents based on the sea water temperature patterns as shown below in Figure 6.

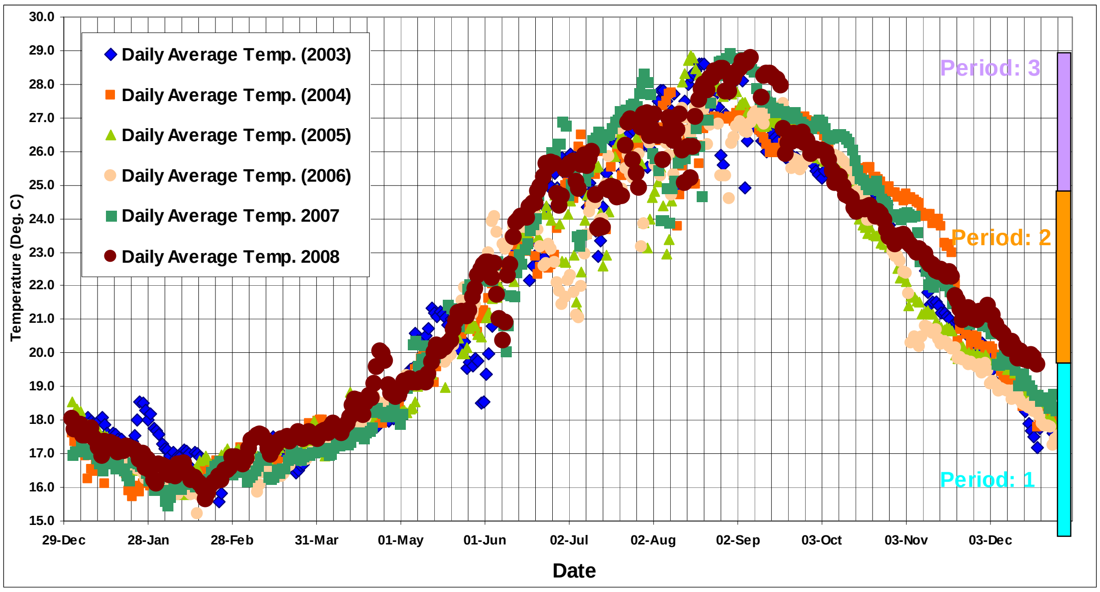


Figure 6: Sea water temperature variations – basis of antiscalant dosing.

Based on the sea water temperatures the mode of plant operation was divided in three periods:

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

The Larnaca Desalination Plant has been investigating with Thermphos in a joint effort the selection of the appropriate antiscalant and optimum dosing as a function of sea water temperature range periods shown above. Each period was defined with a different mode of operation where various plant operational parameters had different values e.g. Flocculant dosing, SDIs, R.O. process feed pressures, DPs, Recoveries, water quantity and quality, 2nd R.O. stage operation etc.

6.1 First R.O. Stage antiscalant considerations

As a first step for investigating potential scaling species sea water analyses were made at different times. Typical results are shown in Table 1 below. In addition other parameters considered include:

- seasonal temperature variability (from 15°c to 30°c),
- sea water composition,
- pH and operational plant conditions

Monitoring normalised data, membrane autopsies as well as visual tests where also helpful to assess indications of membrane scaling.

Parameter	Units	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 SO4--	**3.400**
Bicarbonate	mg/l HCO3-	**128**
Fluoride	mg/l F-	**2**
Sodium	mg/l Na+	**11.670**
Potassium	mg/l K+	**308**
Calcium	mg/l Ca2+	**599**
Magnesium	mg/l Mg2+	**1.453**
Boron	mg/l B	**5**
Iron	mg/l Fe	**<0,05**
Silica	mg/l SiO2	**0,4**

Table 1: typical LDP sea water feed analysis

In order to determine the parameters where scaling could occur, the values of saturations indexes 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 consideration the operational conditions for the specific RO stage. For the seawater composition (see Table 1). As well the pH, temperature, alkalinity, calcium content, TDS, etc, were taken into account. The results of the investigation or LDP are shown in Figure 7 where S&SDI is shown as a function of sea water temperature and pH.

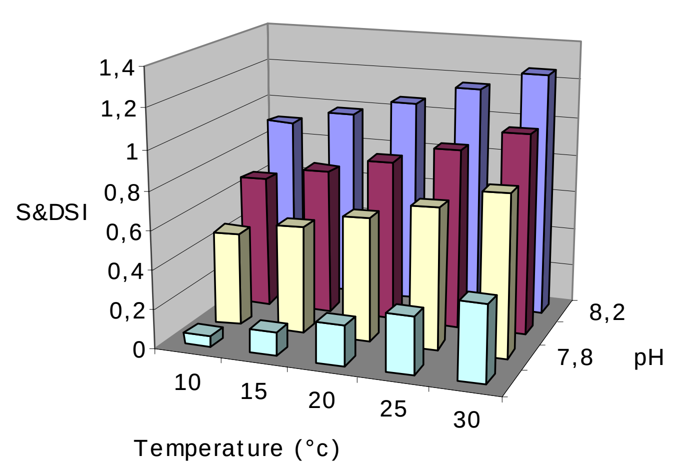


Figure 7: Calculated S&DSI values of LDP (1st R.O. stage) versus pH and sea water temperature.

As a general rule of thumb, antiscalant is required whenever the S&DSI is higher than 0.5. At natural sea water pH of 8.2 and for the sea water temperature variation of 15 – 30 oC, the untreated S&DSI values for the 1st R.O. stage of LDP are ranging between 0,9 to 1,3 (see blue bar graph above). Therefore, antiscalant is required for the 1st stage all the year round.

Based on saturation index calculations, operational parameters of LDP and potential scaling thermPhos selected a phosphonate based antiscalant referred to as 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 R.O. process of LDP in a safe mode w.r.t. calcium carbonate scaling potential. SPE0111 is classified as non-hazardous and is complying with EU Standard for drinking water plants. The dosing rate for the initial trial period under the most severe conditions (pH, temperature) was chosen and a trial was conducted while monitoring the R.O. 1st stage process. The trial was initiated in March 2007 and successfully completed 12 months later with no evidence of scaling based on the historical process data of the plant. Membrane autopsies of rear membranes with visual and other tests where also helpful to assess potentials for scaling.

6.2 Second R.O. Stage antiscalant considerations

The performance of the optimised 1st R.O. stage was such that the second R.O. stage was not required for more than 6 months of the year while meeting all the water quality and quantity contractual 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 R.O. stage was required to operate in order to maintain the water quality requirements of boron. The permeate from the first pass is split into low salinity permeate (front and rear of the pressure vessel) and high salinity permeate from the back of the vessel (5). The high salinity permeate was sent to the second R.O stage. Before entrance into the second stage the pH was elevated by the 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 as for the 1st R.O. stage.

The performance of SPE0111 had to specifically address more the issue of brucite scaling. Laboratory tests were carried out in order to determine optimum antiscalant doses 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 Figure 8 below.

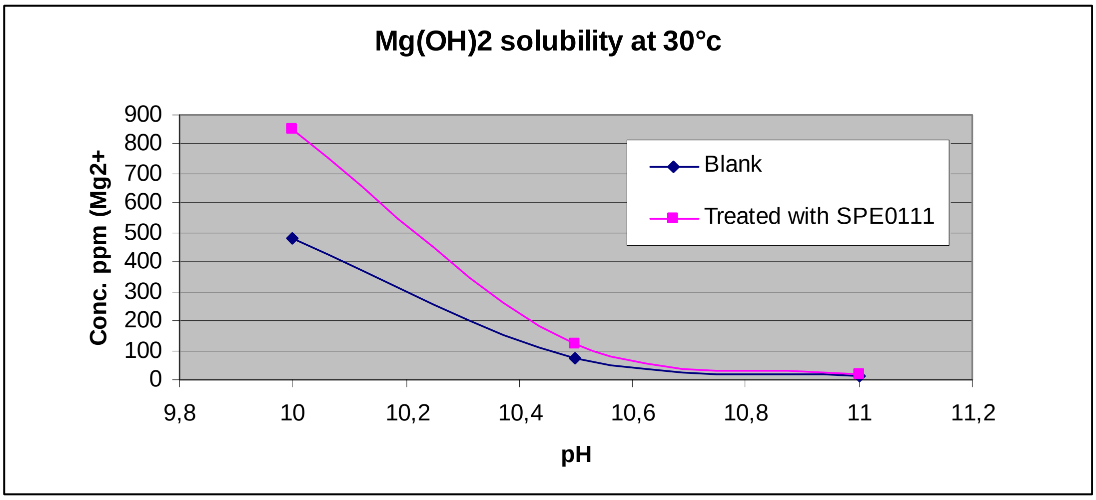


Figure 8: Effect of SPE0111 on the solubility of brucite.

As Figure 8 indicates SPE0111 is able to control brucite precipitation by increasing the solubility of it by approximately two fold in conditions of he second stage at the operating pH range and 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 i.e. no scaling was recorded nor increased pressure drop of the 2nd stage during its operation. However, this trial has to be repeated specially at the highest sea water temperatures (above 28oC) and pH to establish confidence.

7.0 1st stage field trial of applying and optimising antiscalant dose

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

7.1 Analytical method for SPE0111 determination

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

	SPE 0111		**SPE 0111**	
TRAINS	**Start of trial**		**Results of later date**	
	Analyzed	**Calculated**	**Analyzed**	**Calculated**
Train A				
Brine (ppm antiscalant)	2,72	2,36	2,66	2,35
Feed (ppm antiscalant)	1,55	1,26	1,37	1,26
Recovery (%)	46,60%		46,40%	
Train C				
Brine (ppm antiscalant)	2,41	2,33	2,59	2,32
Feed (ppm antiscalant)	1,30	1,26	1,40	1,26
Recovery (%)	46,00%		45,70%	
Train E				
Brine (ppm antiscalant)	2,59	2,39	2,66	2,39
Feed (ppm antiscalant)	1,44	1,26	1,40	1,26
Recovery (%)	47,30%		47,30%	

Table 2: Antiscalant analytical results using spectro – photometric method

The ratio of brine and feed analytical values was monitored on a regular basis for each trains and this was done to check for any "loss" of antiscalant as a sign of a potential scaling. The average value of such ratio was, through the trial period, between 95% to 105%. With such results and taking into account the fluctuations in operational parameters and accuracy of analytical method it was considered that the correct antiscalant dosing was made and no scaling potential was evident. However for cost effectiveness the dosing of the antiscalant requires optimisation depending on the seasonal and plant operation variations.

7.2 Antiscalant performance monitoring

During the field trial the trains performance was monitored using the data from the SCADA on-line system where parameters such as DP feed/brine, production rate, permeate quality, recovery, water quality etc were recorded. Also normalised values were calculated to support the 1st R.O. 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 separately at different times of the year, taking into consideration key factors such as the sea water temperature, membrane changes in trains etc.

In Figure 9 a comparison of delta pressure of the six trains is made after 12 months of the field trial.

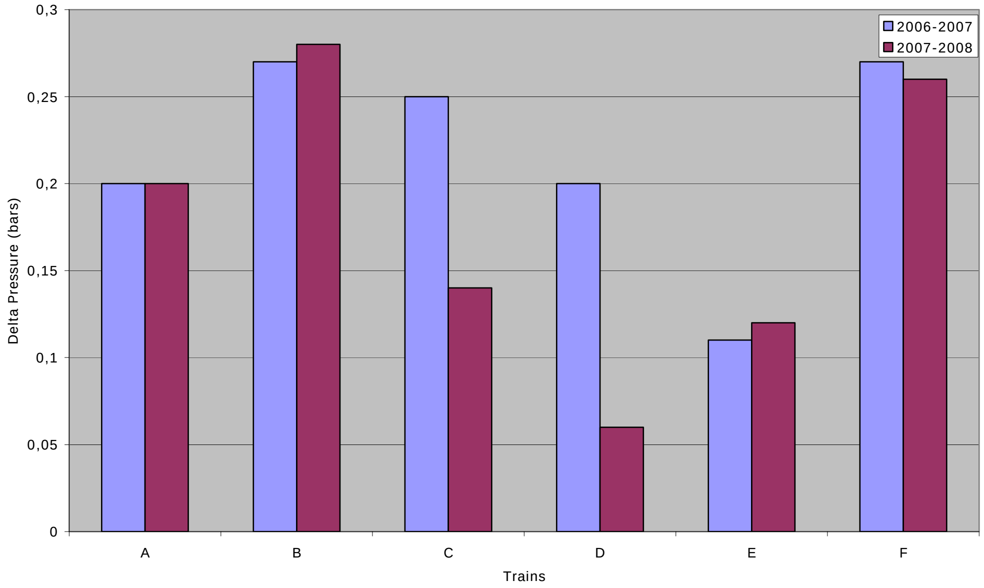


Figure 9: Delta Pressure of all trains during the same period of time for different years

The results show that despite that after one year of operating using the SPE0111 antiscalant, there is no increase in the pressure difference of the Trains, where normally after one year of operation DP should show some increase. This can suggest that the SPE0111 antiscalant used 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 assist to minimise increases of DP of the trains. So, in conclusion the antiscalant used (in conjunction with the above membrane performance - maintained by membrane changes and cleaning) is functioning well to avoid scaling of the membranes at the high sea water 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 sea water temperature profile was divided into three periods of modes of plant operation as described in section 6.0. For the 1st RO stage, for each mode of operation based on the three operational periods, an optimum dosing was recommended as shown in Figure 11 below.

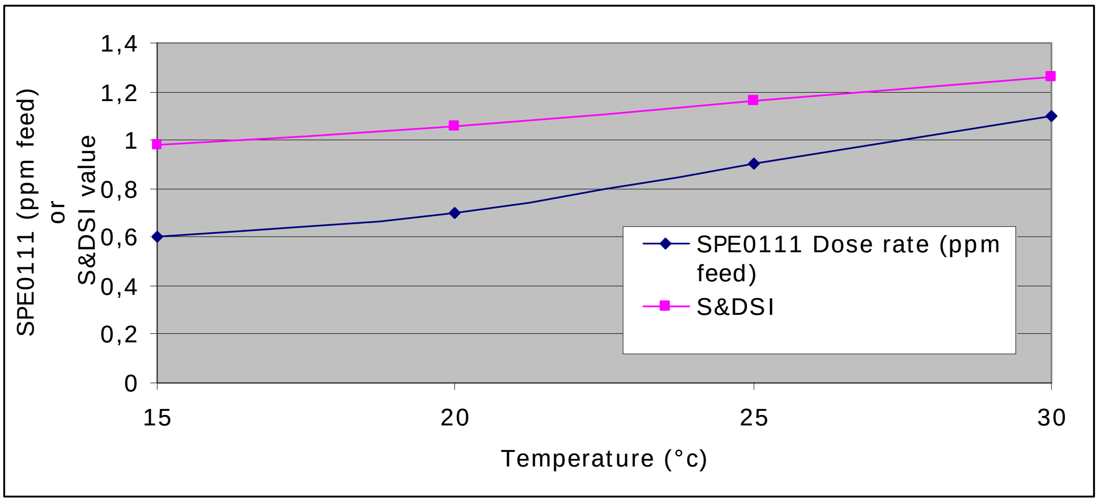


Figure 11: Dose rate of SPE011 in the feed versus mode of operation and S&DSI.

The dosing of the antiscalant was based on the methodology described above. The actual dosing optimisation at different sea water 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 sea water temperature and pH – seasonal mode of operation of the plant which can result in cost effective optimization of antiscalant.

8.0 Conclusions

The Larnaca Desalination Plant 1st and 2nd R.O. stage are operated at a range of sea water feed temperatures from 16 – 30oC and increased sea water pH. The need for the use of cost effective, well performing antiscalant was thus essential.

In co operation with thermPhos a methodology was implemented to select appropriate antiscalant as well as optimise the dosing as a function of sea water temperature and pH. This minimised the potential for scaling and operation of both 1st and 2nd R.O. stages at elevated pH values without scaling. The objective for improving boron removal of the membranes was achieved, enhancing the overall plant performance.

The thermPhos antiscalant SPE011 tested for a year 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 to occur on the membranes.

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

9.0 References

(1) M. Faigon, D. Hefer - Boron rejection in SWRO at high pH conditions versus cascade design, Desalination 223 (2008) 10-16
(2) E, Koutsakos, D. Moxey – Larnaca Desalination Plant -from an efficient to an effective plant operation – 2007 EDS Conference, Halkidiki, Greece, submitted.
(3) E, Koutsakos, D. Moxey - More water less energy and reduced CO2 emissions – the Larnaca Desalination Plant – Presented at Euromed 2009, Dead Sea, Jordan.
(4) E. Koutsakos, K. Savvides – Lazrnaca Desalination Plant opertation – A client contractor perspective, Joint paper with Client, Desalination 184 (2005) 157-164
(5) C.Bartels, S.Cioffi, S. Rybar, M. Wilf, E. Koutsakos - Long term experience with membrane performance at the Larnaca Desalination Plant- 2007 EDS Conference, Halkidiki, Greece, submitted.
(6) E. Koutsakos, D. Moxey - Membrane Management System - Desalination 203 (2007) 307-311
(7) Memento Techniques de l'Eau – Dixième Edition – Degrémont – ISBN 2-7430-0717-6, pp. 218
(8) Standard Practice for Calculation and adjustment of the Stiff & Davis stability index for reverse osmosis - ASTM D 4582-91 (Reapproved 2001)