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The impact of sulphuric acid replacement by a phosphonate-based antiscalant on operational costs of seawater desalination

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ABSTRACT

The operation and maintenance of a seawater desalination plant have many challenges. One of the major challenges is to ensure the economic viability while complying with all the terms of the operation and maintenance contract, hence the constant quest for cost savings. One area for potential improvement is to rethink or optimize the use of chemicals and in particular the use of sulphuric acid. Sulphuric acid is used to lower the pH of feed water in order to reduce the risk of mineral precipitation on the reverse osmosis membranes. Simply eliminating sulphuric acid will result in a substantially higher operating pH and an associated increased risk of mineral precipitation. Managing this risk involves the injection of a properly selected high performance phosphonate-based threshold scale inhibitor. This article describes the details of a field trial in a two-pass seawater desalination plant during which sulphuric acid was phased out and replaced by a phosphonate- based antiscalant. The results show that the critical operating parameters remain stable, indicating the successful prevention of scale formation, throughout the trial period during which sulphuric acid was replaced by a phosphonate-based threshold scale inhibitor. A holistic approach was used to understand the full impact of the replacement of sulphuric acid by a phosphonate-based threshold scale inhibitor on the operating costs of this seawater desalination facility.

Keywords: Desalinization; Desalination; Operation and maintenance; Antiscalant; Sulphuric acid; Cost saving

1. Introduction

For more than 35 years, desalinization has been commercially used for the production of good quality irrigation and drinking water. One method of desalination is filtration through a semi-permeable membrane called the reverse osmosis (RO) process, involving high energy demanding pressure pumps, chemical treatments and qualified labour. The use of chemical products during the pre- and post-treatment of the water is essential to ensure smooth process operation and fulfil the water quality requirements set by the clients or law.

The operation and maintenance of a desalinization plant constantly look for operational cost savings which do not negatively impact the performance of

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the plant. In a seawater reverse osmosis (SWRO) plant, energy is well known to be the first item to consider for cost-saving efforts. Once energy has been optimized, the cost evaluation efforts are focused on other operation expenditures such as chemical reduction and optimization.

2. Desalinization costs

The production of potable water via SWRO is currently commonly used in all regions facing water deficits. Today's production price of drinking water produced by SWRO ranges from 0.4 to 1.6 €/m^3 [1]. The cost breakdown of SWRO product water is difficult to estimate because most operators keep data confidential [2]; however, some of these costs have been described in literature [1–3]. As a general rule, operational costs are very site-specific [2]. Despite the variability in the values, due to site specific situations, the major costs are due to fixed costs and to electric power: the fixed costs being related to public subsidies, the cost of the land and the cost of capital, while the variable costs can be related to local regulations, the labour costs, energy supply and consumables availability and pricing.

A global overview of operational costs is described in various publications (Figs. 1 and 2). Once the operation team has optimized the energy consumption of the plant, other points of attention for cost saving like chemical usage in particular sulphuric acid could be studied.

This article describes the usage of a phosphonate-based antiscalant in cost- effective replacement of sulphuric acid. As such, it has an impact on a part of the chemical budget.

3. Scale control

In RO, the risk of precipitating salts is proportional to the solubility of salts along the membrane. The solubility of salts depends on the concentration of cations and anions, the temperature, ionic strength and the pH of the water.

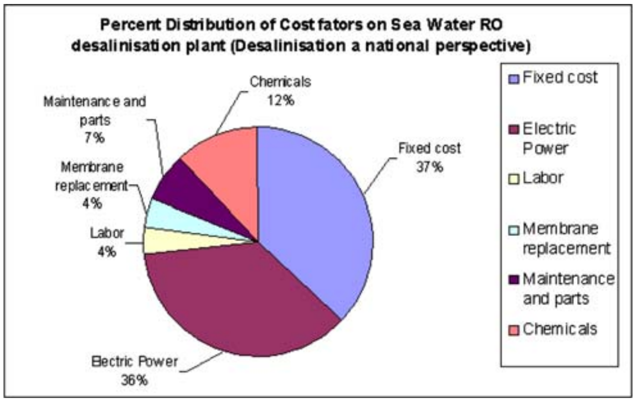


Fig. 1. Source – Desalinization: a national perspective (2008) [2].

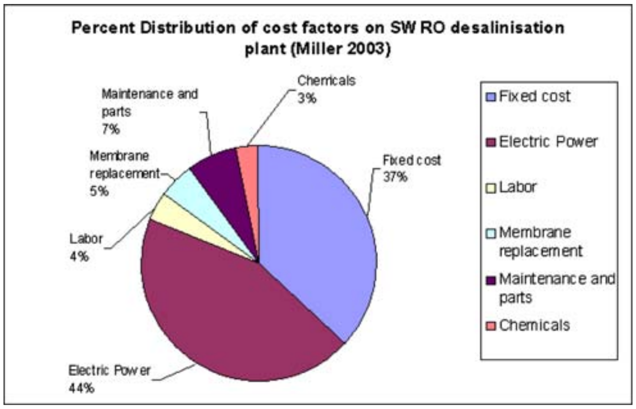


Fig. 2. Source Miller (2003) [3].

In SWRO, mineral scale issues are mainly related to calcium carbonate and magnesium hydroxide. In a two-pass boron removal (BR) system (SWRO design studied in this article), the calcium carbonate scale can occur at both pass of the process, while the magnesium hydroxide normally represents a scaling risk only on the second pass. One reason for the high scaling tendency in the second pass is that the feed water pH is above 9 for efficient boron rejection, which is ideal for the formation of magnesium hydroxide and calcium carbonate precipitates [4]. Calcium carbonate scaling in the first pass is typically prevented by an acidification of the feed water, the injection of a scale inhibitor or a combination of the two. Scale formation is typically controlled by an efficient scale inhibitor.

3.1. Feed water acidification for scale control

In order to avoid calcium carbonate precipitation, acidification can be performed upstream of the RO unit.

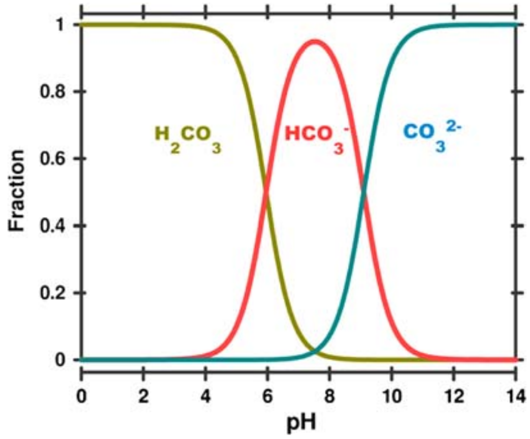


Fig. 3. Carbonic acid speciation.

The natural pH of seawater is around 8.1, which is also near the set point for carbonate predominance. Fig. 3 shows the dependency of calcium carbonate solubility towards pH. This information proves that acidification of sea water to pH 7 reduces the potential for calcium carbonate scale formation on the membrane. Due to a relatively low cost, sulphuric acid is the most commonly used chemical for acidification of SWRO systems [5]. However, due to sulphuric acid price fluctuation and issues due to local logistics and handling, some operators are looking for alternatives to replace sulphuric acid.

3.2. The use of threshold inhibitor for scale control

Antiscalants act by inhibiting the crystal formation of salts, modify growth structure and act as a dispersant for eventually formed crystals. The functionality of effective antiscalants, like phosphonates, should be based on the following functional properties:

- *Threshold inhibition*. The ability of small amounts of scale inhibitor to keep larges quantities of scale in solution (i.e. sub-stoichiometric conditions).
- *Sequestration (or chelation)*. Sequestration is the formation of a stable water soluble complex of a cation with the antiscalant.
- *Dispersion*. Prevention of further agglomeration or further "lumping together" of precipitated solids in the solution.

The combination of these properties allows the antiscalant to be highly effective in preventing the precipitation of scales.

The selection and optimal dose rate of a threshold scale inhibitor is determined by the pH of the feed water, ionic composition, temperature and a variety process conditions.

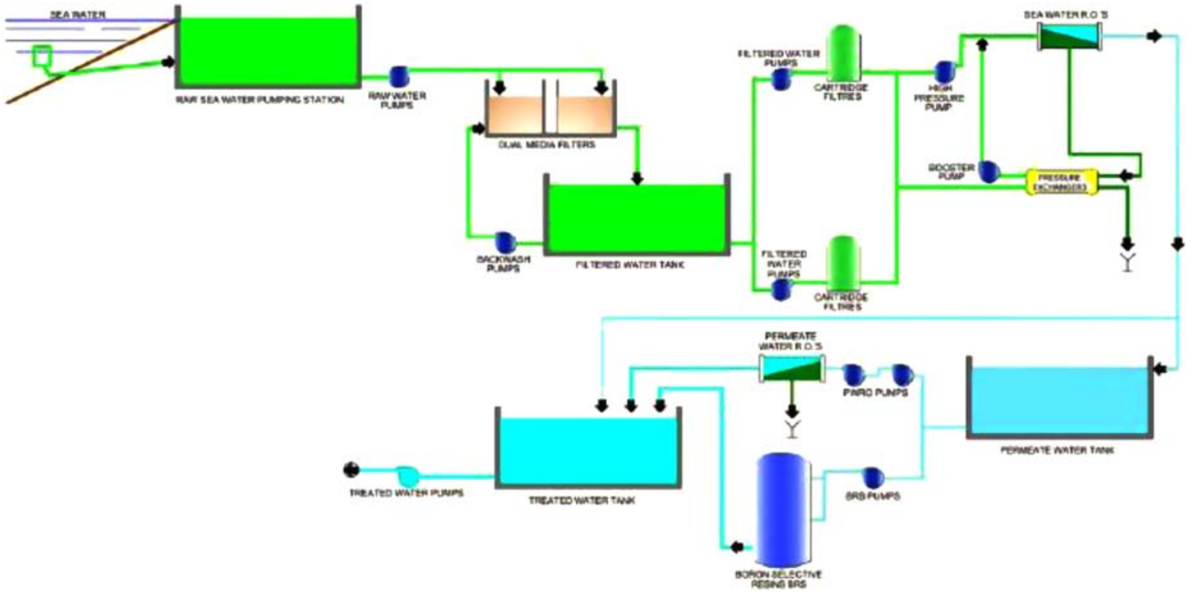
4. Dhekelia plant description

The Dhekelia desalination plant is located at the south-east end of Cyprus. The contractual plant capacity is 60.000 m^3/day and treats Mediterranean seawater with a total dissolved solid (TDS) of 41,500 ppm [6]. The operation of the Dhekelia desalinization plant began in April 1997.

During the last 15 years, a lot of process adjustments and system modifications were done in order to improve the operational costs, comply with all contract obligations and EU regulations, and keep up with current technology. Two of the major changes were the installation of a BR system and the installation of an energy recovery system [6].

4.1. Intake and pre-treatment

The seawater is drawn from a 600 m long, undersea pipe to a reservoir. After chemical addition for pH correction and coagulation by the addition of sulphuric acid to pH 7.0 and Ferric Chloride, the first step is coarse filtering of the water. The water is then further filtered through dual media filters. The filtered water is then passed through a 1 μm cartridge filter after which it is sent to the RO's first pass, where the permeate water is divided into three streams [7].



4.2. BR system

The SWRO first pass permeate is split in three flows. Each permeate flow will get a specific treatment. Two of the flows will go to the BR system; the third flow goes directly to the remineralization phase.

The BR system consists of two lines that were installed with the objective to achieve the contract requirements of 0.5 ppm maximum of boron in drinking water. The first line is an ion exchange system based on a boron-specific resin. The second line is a second pass BR RO system. Both outlets of these lines achieve very low residual boron and are mixed with the third line (remineralization) in order to comply with the required 0.5 ppm maximum of boron.

The performance of the RO system is affected by the feed water temperature, resulting in two periods of operation: a "summer mode" (from May to November) with feed water around 23–32°C and a "winter mode" (from December to April) with feed water around 15–22°C. For high TDS seawater, boron rejection by the membrane is better at lower temperatures [4]. The lower temperatures allow the plant not to require the second pass to be operated in the winter mode. The "summer mode" is characterized by the operation of the second pass BR system when seawater is above 25°C. The BR ion exchange system is operational irrespective of the water temperature.

4.3. Post-treatment and remineralization

In order to comply with EU regulations, the RO and ion exchange downstream permeate need some post-treatment chemical additions as it is very corrosive due to a low ionic content. This remineralization phase consists of the addition of CO_2 and lime through a lamellar saturator. Disinfection by chlorine addition is finally done before the water enters into the final storage tank [7].

5. Description of the trial

The objective of the trial was to fully replace the sulphuric acid used for scale control by a phosphonate-based antiscalant and check the impact on the performance and operational cost of the plant. The concept is that large doses of acid are more expensive to buy and more risky for handling and logistic perspective than smaller doses of antiscalant.

On the basics of the analysis of the seawater composition and the operational parameters of the Dhekelia plant, the SPE0111 product from ThermPhos was selected through the Corola T product selection software as the most appropriate scale inhibitor to operate under those conditions.

In order to reduce the risk of a sudden switch to all antiscalant, the trial was organised into three phases. The three phases are characterized by specific feed water pH targets and corresponding recommended dose level of SPE 0111 for each feed water pH (Table 1).

The progressive replacement of sulphuric acid by the antiscalant increases the pH closer to the feed water's initial pH of around 8.1. Without the dose of SPE 0111, the initial feed water pH would cause severe mineral scaling conditions on the membranes.

The trial started on May 2011, for a duration of about six months.

6. Results

6.1. RO operational parameters monitoring

The normalized parameters, for permeate flow, differential pressure across the membranes and salt passage were followed up on a daily basis. As Fig. 4 demonstrates the change in the pH upstream of RO had no negative impact on the operation. We find no evidence of scaling as can be verified by the normalized data, and the SPE 0111 was proven to be an effective antiscalant for this plant in the absence of sulphuric acid.

6.2. Operation cost analysis

During the trial period (summer mode), the operating costs of chemical reagents were compared

Table 1
Phases for replacement of acid addition by antiscalant

	pH	Dequest SPE0111 Dose
Phase 1	7–7.5	0.7
Phase 2	7.5–7.8	1.1
Phase 3	7.8–8.1	1.3
Normal operation	8.1	1.3

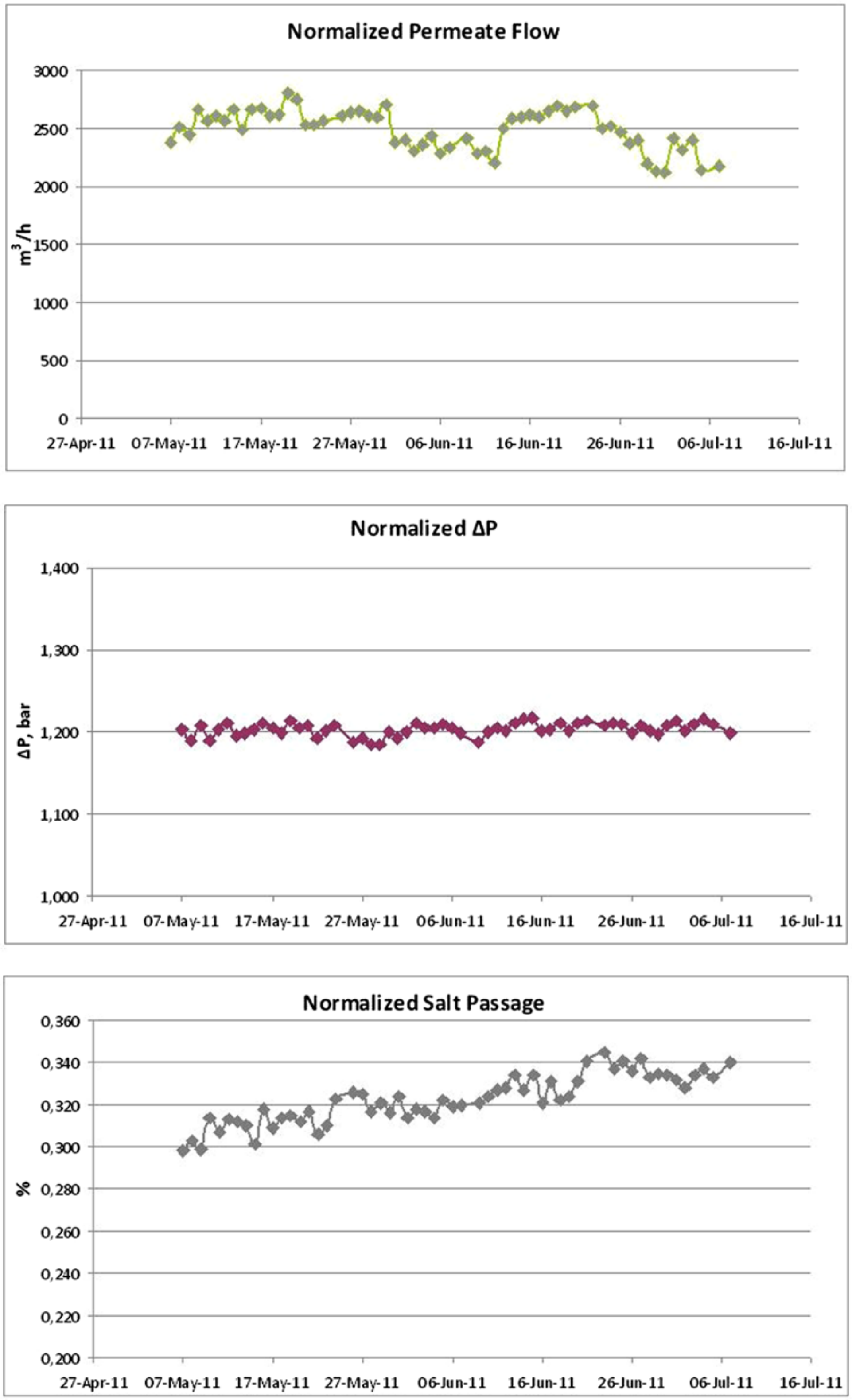


Fig. 4. Normalized parameters.

against the operating costs of the year before (i.e. when they used sulphuric acid over the same period). The cost was compared on a €/m^3 water production. The pre-treatment coagulant reagent is not included in the comparison because it is unchanged. The use of chemicals reagents is described in Tables 2 and 3.

Table 2
List of chemicals used for cost comparison in sulphuric acid setup

Terms	Use	Target
H_2SO_4 acidification	Acid injection to avoid scaling on first pass RO	pH 7
NaOH 100% second pass BR	Soda injection before second pass	pH > 9
Antiscalant	Avoid scaling on second pass PWRO	1.5 mg/l in the feed water
H_2SO_4 regeneration	Regeneration of BR ion exchange resins	On volumetric cycle
NaOH 100% regeneration	Regeneration of BR ion exchange resins	On volumetric cycle
CO_2 remineralisation	Remineralisation phase	
Lime remineralisation	Remineralisation phase	

Table 3
List of chemicals used for cost comparison in antiscalant setup

Terms	Use	Target
Antiscalant	Avoid scaling on first pass SWRO	1.5 mg/l in the feed water
H_2SO_4 regeneration	Regeneration of BR ion exchange resins	On volumetric cycle
NaOH 100% regeneration	Regeneration of BR ion exchange resins	On volumetric cycle
CO_2 remineralisation	Remineralisation phase	
Lime remineralisation	Remineralisation phase	

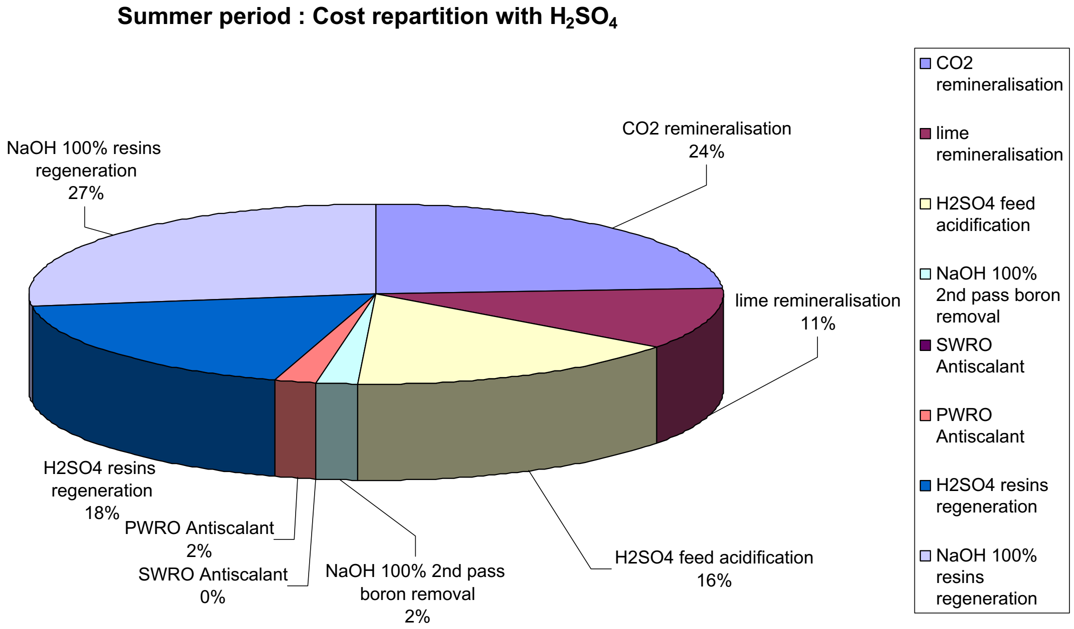


Fig. 5. Cost repartition with sulphuric acid.

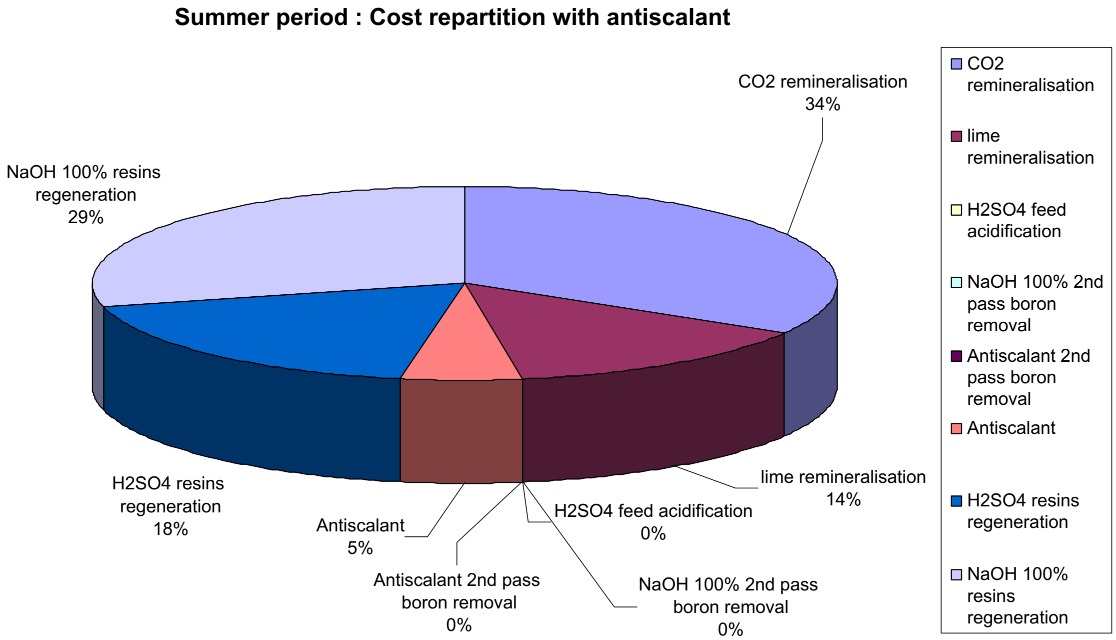


Fig. 6. Cost repartition with Antiscalant.

6.2.1. Cost breakdown during the trial period

Figs. 5 and 6 show the chemical cost breakdown respectively, with the sulphuric acid setup and the phosphonate-based antiscalant set-up.

In Fig. 5, the total sulphuric acid cost represents 34% of the budget. Sulphuric acid is used not only for acidification of feed water but for ion exchange resins regeneration as well. Even if antiscalant for the first pass (5% of total budget in Fig. 6) replaces all of the sulphuric acid in the pretreatment, it would still be needed for the ion exchange resin regeneration. The sulphuric acid for ion regeneration still represents 18% of the total budget.

The pH difference between the two conditions has two major consequences:

- As expected, the RO second pass used for BR can be stopped in the antiscalant setup because the boron rejection from the first pass was increased by the higher feed pH. This also leads in the suppression of the soda injection before the second pass and of course the antiscalant dosing. The net results are additional savings.
- Secondly, the remineralization is impacted. Indeed, the data confirmed that a higher feed pH results in a decrease of available CO_2 in the permeate before the remineralization. This drop needs to be compensated by higher CO_2 addition in the last step of remineralization. This impact is reflected by the higher CO_2 costs as shown in Fig. 6.

6.2.2. Operational cost comparison

Fig. 7 shows the cost comparison of the impacted items between the antiscalant setup and the sulphuric acid set-up.

This cost comparison shows the importance of the energy cost savings with the antiscalant set-up. The cost savings on chemicals achieved by stopping the feed water acidification and soda addition before the

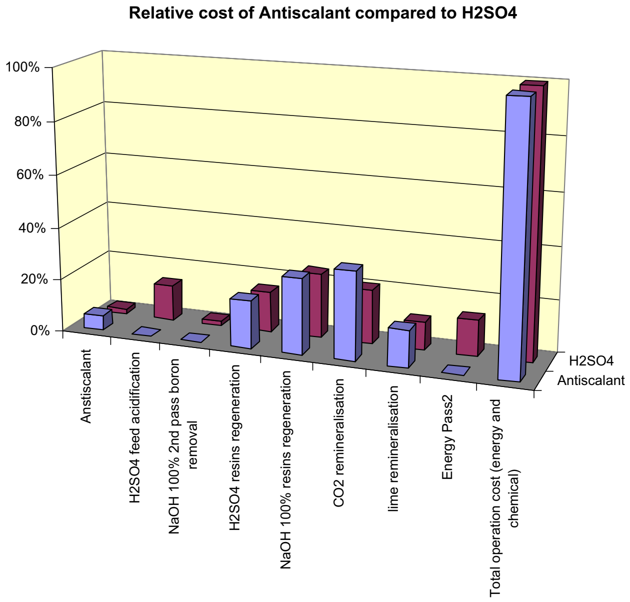


Fig. 7. Cost comparison between antiscalant set-up and H_2SO_4 set-up.

second pass is not sufficient to compensate for the higher consumption of remineralization chemicals in the antiscalant set-up. The higher consumption of carbon dioxide leads to an operational cost gap between the antiscalant and the sulphuric acid set-up. This gap is closed by the energy savings coming from ceasing operation of the second pass.

The ion exchange process seems to consume more reactive in the antiscalant mode and need to be further investigated.

The trial shows that in this particular SWRO plant, the total operational bill of the antiscalant set-up and sulphuric acid set-up is very similar. This is mainly driven by the fact that in the antiscalant set-up the increased costs associated with the remineralization are traded off by energy savings resulting from ceasing second pass operation.

7. Conclusions

This trial shows that in this specific two-pass SWRO plant, sulphuric acid can be replaced by a phosphonate-based antiscalant without affecting its operation and without increasing the operational costs.

The elimination of sulphuric acid brings multiple benefits:

- Sulphuric acid is a dangerous product. Removing sulphuric acid reduces transport and handling risks and improves overall safety.
- Sulphuric acid is a commodity-based product. Removing sulphuric acid will make the plant less exposed to operational cost fluctuations.
- Replacing sulphuric acid allows for elimination of a second pass under BR conditions. Removing sulphuric acid will reduce the footprint of such SWRO installations.

Since each SWRO plant is unique, the results of this study cannot be transposed to a plant in another location. Differences in plant design characteristics, operating conditions, energy and other consumables costs imply that each plant has to be studied in detail before drawing conclusions on the feasibility to replace sulphuric acid by a phosphonates-based threshold scale inhibitor. The real cost impact will be site-specific and trials and calculations will have to be carried out on the individual plant level to provide a successful cost-saving exercise.

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