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## Importance and impact of post treatments on design and operation of SWRO plants

N. Delion\*, G. Mauguin, P. Corsin

*GLS, 6A avenue de l'Europe, 78 117 Toussus le Noble, Paris, France  
Tel. +33 (1) 39561414 ; Fax +33 (1) 39562929; email: n-delion@gls.fr*

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### Abstract

The permeate quality of seawater reverse osmosis (SWRO) plants is suitable neither for drinking water nor for irrigation purposes. Thus, treatments must be adjusted to decrease boron concentration and post-treatments are required to improve water mineralization in order to correct its corrosiveness. Several chemical strategies were studied, and the evolution of different indicators including Leroy and Larson ratios were analyzed to evaluate the quality of the product water before distribution. Corrosive quality of the permeate remains the critical factor because of its high chloride concentration. Different strategies can be used to produce drinking or irrigation water from seawater. Chemicals added to the permeate must be carefully chosen if one pass only is used for reverse osmosis. In the case of two passes, the problem is less critical, but still remains important.

*Keywords:* Seawater; Reverse osmosis; Post-treatments; Leroy; Larson; Boron; Corrosion; Mineralization

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### 1. Introduction

It is now clear that pre-treatments are very important for seawater reverse osmosis (SWRO) desalination plants and this is easily understandable. On the other hand, the importance of post-treatments and their influence on SWRO plant design are less obvious to everyone.

The quality of the produced permeate does not meet all end-use requirements, hence the need for its additional treatments.

This paper will discuss seawater desalination plants designed for producing water for drinking and for watering private or public gardens. We will not cover post-treatments required for the production of industrial waters, because of their specific end-uses (process, cooling circuits, boiler

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\*Corresponding author.

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feed, etc.) which generally dictate point of use treatments.

Furthermore, post-treatments alone may not, in some instances, meet all the requirements for the treated waters. Then, one has to consider working on the performance and the possible combinations of RO membranes when first designing the plant, as well as while operating it.

## 2. Characteristics of permeate

Mediterranean seawater will be used to define the average chemical characteristics of permeate, as it represents a good compromise between open seas (Atlantic Ocean), with low temperature and salinity, and closed seas (Red Sea) with high temperature and salinity.

Table 1 gives main characteristics of raw Mediterranean seawater, which will be the standard for this study, and acidified seawater entering membranes (sulphuric acid is used).

Elements such as barium, strontium, fluorides, bromides, silica have been neglected because of their low concentration in seawater and consequently in the permeate. Table 2 gives the chemical content of permeate produced under the following conditions: model of membranes: TFC; configuration: spiral wound; fouling factor 0.85; net feed pressure 65 bar; recovery 40%. As the cut-off point of RO membranes is very low (<0.001  $\mu\text{m}$ ) water

Table 2

Permeate analysis obtained from reference seawater

	Non acidified feed	Acidified feed
Cations, mg/l as ion		
Ca <sup>2+</sup>	1.80	1.80
Mg <sup>2+</sup>	6.70	6.70
Na <sup>+</sup>	119.20	119.20
K <sup>+</sup>	6.60	6.60
Anions, mg/l as ion		
HCO <sub>3</sub> <sup>-</sup>	2.30	1.90
SO <sub>4</sub> <sup>2-</sup>	10.90	11.00
Cl <sup>-</sup>	203.30	203.50
Total boron, mg/l	0.44	0.55
pH	5.57	4.95
Free CO <sub>2</sub> , mg/l	2.90	21.90
TDS, mg/l	350.80	350.70

is perfectly disinfected. Permeate contains over 92% of sodium chloride, which is the main characteristic of a permeate produced from seawater. As for boron, the WHO guideline is still respected if raw water is not acidified. In that case, particular attention should be paid to chemical pretreatment in order to avoid calcium carbonate and magnesium hydroxide precipitation on membranes. Sulfuric acid must be replaced by a scale inhibitor.

Table 1

Characteristics of reference seawater, before and after acidification

Cations (mg/l as ion)	Non acidified feed	Acidified feed	Anions (mg/l as ion)	Non acidified feed	Acidified feed
Ca <sup>2+</sup>	450.00	450.00	HCO <sub>3</sub> <sup>-</sup>	153.00	127.80
Mg <sup>2+</sup>	1410.00	1410.00	SO <sub>4</sub> <sup>2-</sup>	2700.00	2721.20
Na <sup>+</sup>	11,849.00	11,849.00	Cl <sup>-</sup>	21,500.00	21,500.00
K <sup>+</sup>	440.00	440.00			
Total boron	5.5 mg/l				
pH	8.10 (7.00 for acidified feed)				
Free CO <sub>2</sub>	2.90 mg/l (21.90 mg/l for acidified feed)				
TDS	38,502.00 mg/l (38,498.00 mg/l for acidified feed)				

### 3. Quality required at the outlet of desalination plants

#### 3.1. Quality for drinking water production

Distributed water should meet the requirements defined by national or international standards, especially Total Dissolved Solids (TDS) and concentration of specific ions. Following conclusions of section 2, attention is paid to sodium and chlorides. Table 3 gives standards from European Union (Directive 98/83/CE of 3 November 1998) and World Health Organization WHO.

Table 3  
Required and recommended values from the European Union and WHO

	European standard	WHO <sup>1</sup>
Chlorides, mg/l	250	250 <sup>2</sup>
Sulfates, mg/l	250	250
Sodium, mg/l	200	200 <sup>3</sup>
Boron, mg/l	1	0.5 <sup>4</sup>
Conductivity, $\mu$ S/cm	2500	—
TDS, mg/l	—	<600: good palatability <sup>5</sup> >1200: unpalatable <sup>5</sup>
pH	6.5–9.5	—

<sup>1</sup> Levels likely to give rise to consumer complains or guideline value for boron

<sup>2</sup> Reasons for consumer complains: taste, corrosion

<sup>3</sup> Reasons for consumer complains: taste

<sup>4</sup> Provisional guideline value, available information on health effects is limited

<sup>5</sup> Guideline value, which is not health-based, has been proposed

#### 3.2. Quality for networks and equipment protection against corrosion

##### 3.2.1. Calco-carbonic balance

Various chemical compounds are dissolved in natural water. The main element is calcium carbonate the equilibrium of which depends on interactions with CO<sub>2</sub>. Fig. 1 gives different forms

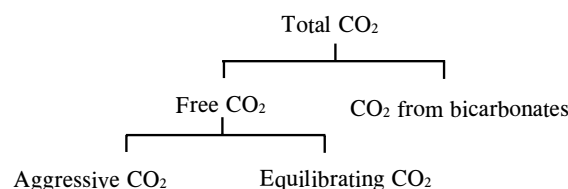


Fig. 1. Distribution of different CO<sub>2</sub> forms in water.

of CO<sub>2</sub> in water. Chemical equilibrium linked to calcium carbonate, called calco-carbonic balance, can be shifted under CO<sub>2</sub> action. Calcium carbonate can be either dissolved (aggressive water) or precipitated (scale forming water). Water at equilibrium neither dissolves nor precipitates calcium carbonate. It is then characterized by its saturation pH, called pH<sub>s</sub>.

The Hoover nomogram presented in Fig. 2 enables to determine pH<sub>s</sub> for water.

It is also possible, using various calculations, to determine if water is aggressive, scale forming or corrosive, using the following ratios: Langelier index (LI); Ryznar index (RI); Larson ratio (LnR); Leroy ratio (LyR); saturation index (SI).

To protect distribution networks and equipment, water should not be aggressive regarding calcium carbonate. Moreover, water should be slightly scale forming to create a protective coat on internal surfaces.

##### 3.2.2. Calco-carbonic balance indexes

###### Langelier index

$$LI = pH - pH_s$$

if LI < 0, water is aggressive; if LI > 0, water is scale forming.

###### Ryznar index

$$RI = 2pH_s - pH$$

It quantitatively defines the aggressiveness or the scaling potential of aerated water. Water of pH<sub>s</sub> of 7 is scalant if RI < 7 and aggressive if RI > 7.

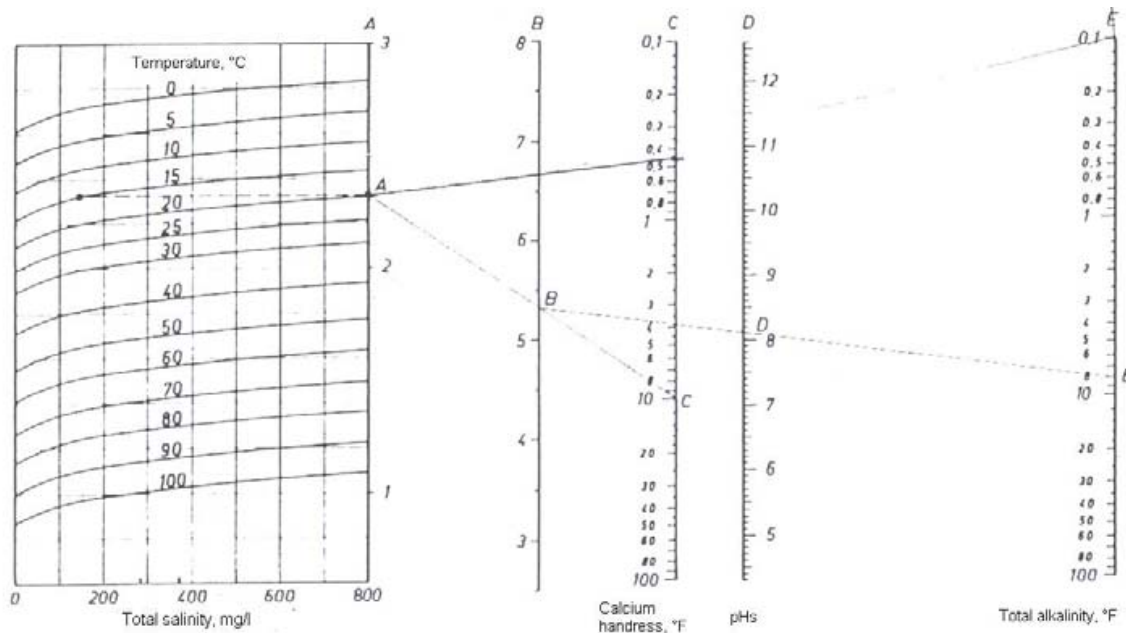


Fig. 2. Hoover nomogram for saturation pH determination.

Saturation index

$$SI = \frac{[Ca^{2+}] \times [CO_3^{2-}]}{K's}$$

where *K's* is the solubility product of calcium carbonate, Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>, mg/l as ion. It is a quantitative kinetic ratio which gives an indication of either the aggressivity or the scaling potential of water: SI < 1: water is aggressive; SI = 1: water is balanced (equilibrium); SI > 1: water is scale forming.

As the Langelier index gives only a qualitative indication, and as the Ryznar index depends strongly on pHs, the saturation index will be used for the rest of the study, as it is the most accurate index. Indeed, the saturation index takes into account the dissolution and precipitation kinetics of calcium carbonate. For remineralized permeate, it should approach 1.2, so that the kinetic of calcium carbonate deposition is faster than the kinetic of corrosion by chloride ions.

3.2.3. Corrosivity indexes

Larson ratio

$$LnR = \frac{[Cl^-] + 2 \times [SO_4^{2-}]}{[HCO_3^-]}$$

The concentrations are in mol/l. It quantitatively represents the corrosivity of water, corrosion being, in that case, due to chloride and/or sulfate ions (Table 4).

This empirical formula is based on many experiments performed by Larson and Skold, who

Table 4  
Corrosive potential of water regarding Larson ratio values

LR	Corrosive potential
<0.2	no potential
0.2–0.4	small potential
0.4–0.5	slight potential
0.5–1	average potential
>1	strong potential

estimated that it should not exceed 0.2–0.3. Other authors assessed that values up to 1 were acceptable.

#### Leroy ratio

$$\text{LyR} = \frac{\text{TAC}}{\text{TH}}$$

Total alkalinity and calcium hardness given in French degree (°F). For small corrosive potential, values should be between 0.7 to 1.3.

#### 3.3. Quality for irrigation water

Three criteria are essential for this application: mineralization, sodium and boron concentrations.

Total mineralization is not essential in case of desalinated water, as it is generally lower than 800 mg/l after post-treatments. Under this level, grass can grow normally.

Nevertheless, sodium, calcium and magnesium concentrations are important as they can change the physical properties of soils, in particular their permeability. A ratio called sodium adsorption ratio (SAR) (Table 5) takes into account mutual effects of these three ions:

$$\text{SAR} = \frac{\text{Na}^+}{\sqrt{\frac{\text{Ca}^{2+} + \text{Mg}^{2+}}{2}}}$$

Na, Ca and Mg in meq/l. For fruit trees, boron is toxic when its concentration is above 1 mg/l. A

concentration of 0.5 mg/l approximately is necessary to avoid marks on fruit, which would mar their appearance.

## 4. Corrective actions on permeate

### 4.1. Corrections for drinking water purposes

Although reverse osmosis eliminates bacteria and viruses, chlorine must be added to water so that its remnant action would protect it from further pollution during post-treatments, transportation and storage. Even if sodium and chlorides have no negative effect on health and their concentrations in product water are under guideline values, the fact that they represent almost the total dissolved solids of water contributes to make it tasteless. To improve the taste of water, ions such as calcium and bicarbonates should be added. At the same time, the water remineralization should not increase concentrations of chlorides and sodium, as their concentrations in permeate already almost reach the guideline values.

Boron concentration in the permeate is close to the guideline value and can sometimes exceed it. Consequently, acid cannot be added in the RO feed, and in some cases, elevation of pH is required by addition of caustic soda for instance. pH increase enables ionization of boric acid and improves its rejection by membranes. Fig. 3 gives an idea of membrane rejection of boron species as a function of the pH, for seawater.

### 4.2. Corrections for protection against corrosion

As explained before, the corrosive potential of water is characterized by two indexes: the Larson ratio and the Leroy ratio. For no corrosion risk, LnR should be <1 and LyR should be between 0.7–1.3. This means that both chloride and sulfate concentrations should be low and bicarbonate concentration should be important. At the outlet of the reverse osmosis units, water is very corrosive. Indeed, the chloride concentration

Table 5  
Effects of sodium on soils depending on SAR value

SAR	Effects of sodium
≤10	No effects — suitable for every kind of soil
10.1–18	Risks of accumulation in case of fine soils — suitable for sandy soils
18.1–26	Risks for every kind of soils — need to use a conditioner and to improve drainage
>26.1	Water not suitable for irrigation

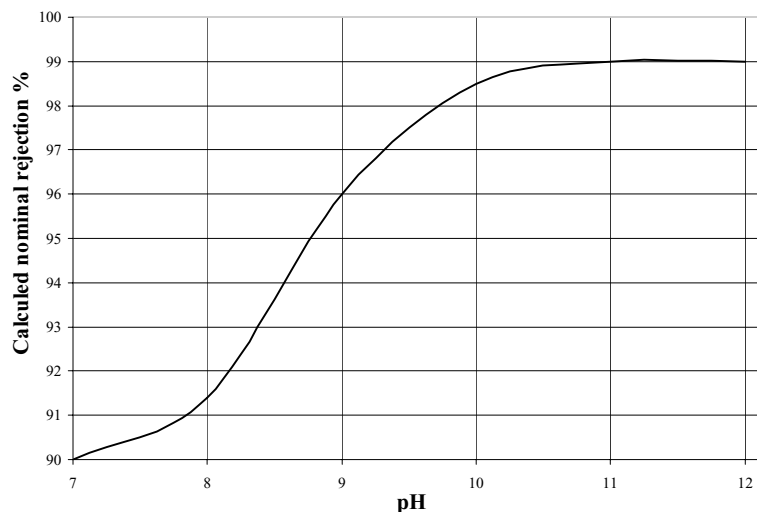


Fig. 3. Boron species rejection at 25°C for seawater.

is very important and concentrations of other ions are very low (except sodium). As it is not easy to decrease the chloride concentration, the total alkalinity should be increased. This will lower the Larson ratio and put the Leroy ratio in the required range.

As we will see later, the optimum Larson ratio value is difficult to obtain without considering a double pass for membranes (seawater membranes for first pass and brackish water membranes for second pass) in order to decrease the concentration of chlorides. As in a first approach the double pass solution is not foreseen, it is necessary to make water slightly scale forming to create a protective deposit on internal surfaces of pipes and equipment. For that purpose, the saturation index should be over 1 and close to 1.2.

#### 4.3. Corrections for irrigation water

If the boron concentration falls under drinking water guidelines, it will consequently meet irrigation standards for private and public garden watering.

One should however check that post-treatments will lead to SAR values compatible with the permeability of soils.

#### 4.4. Conclusions about the post-treatments to be considered

In addition to chlorination, remineralization of the permeate is essential, mainly because of its corrosive properties. Moreover this remineralization improves the taste of water and its suitability for irrigation. Membrane feed water will not be acidified in order to meet the boron guidelines given by the European Union and WHO.

### 5. Remineralization treatments to be considered

#### 5.1. General

Remineralization is accomplished either by filtration or by chemical injection. Filtration is done on calcium carbonate, in calcite form ( $\text{CaCO}_3$ ,  $\text{MgO}$ ) or dolomite form ( $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ), combined with carbon dioxide injection ( $\text{CO}_2$ ). This treatment enables us to obtain water at calcocarbonic balance, sodium carbonate  $\text{Na}_2\text{CO}_3$  is injected then to increase the saturation index up to 1.2. Chemical injection uses sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), calcium chloride ( $\text{CaCl}_2$ ), lime ( $\text{Ca(OH)}_2$ ), carbon dioxide ( $\text{CO}_2$ ).

Calcium sulphate ( $\text{CaSO}_4$ ) will not be discussed here. This chemical allows increasing the calcium hardness of water without increasing the chloride concentration. But using this product is difficult because of its low solubility (1.8 g/l at 20°C).

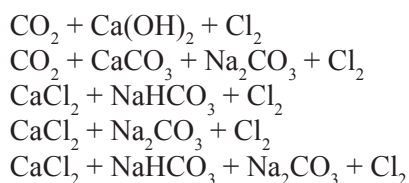
$\text{CO}_2$  stripping is not discussed neither, because:

- if the feed water is not acidified, free  $\text{CO}_2$  concentration is very low and therefore difficult to eliminate by stripping;
- $\text{CO}_2$  can contribute to remineralization of water by bicarbonate formation;
- $\text{CO}_2$  stripping, followed by lime or caustic soda addition, leads to very corrosive and non-buffered water.

### 5.2. Simulations

Simulations have been conducted with LpL Win software, on the basis of standard permeate as defined in Table 2 (without acidification): free  $\text{CO}_2 = 2.9$  mg/l; pH = 5.57; total hardness = 3.20°F; calcium hardness = 0.45°F; total alkalinity = 0.037°F

Several treatments have been studied, using the following chemicals associated to chlorine for disinfection: carbon dioxide  $\text{CO}_2$ ; lime  $\text{Ca}(\text{OH})_2$ ; sodium bicarbonate  $\text{NaHCO}_3$ ; sodium carbonate  $\text{Na}_2\text{CO}_3$ ; calcium chloride  $\text{CaCl}_2$ , in the following combinations:



Each treatment has been optimized to obtain a final saturation index close to 1.2.

The concentrations of chemicals have been first calculated to obtain a calcium hardness as close as possible to 8°F. When one parameter was out of the specifications ( $\text{Na}^+$ ,  $\text{Cl}^-$  concentrations, index, etc.), chemical dosages has been modified in order to correct it. See Table 6 for results.

### 5.3. Comments on the results obtained through various remineralization treatments

Several conclusions can be drawn. Whatever the treatment, a SI of 1.2 is always achieved, without excessive dosage of chemicals. SAR values are always 0, and water obtained could be then used for every kind of soil.

- $\text{CO}_2 + \text{Ca}(\text{OH})_2 + \text{Cl}_2$  (treatments 1 and 2)

Addition of carbon dioxide and lime give a slightly scale forming water (SI = 1.2), without exceeding guidelines for chlorides and sodium. Treatment 1 reaches a final calcium hardness of 8°F. In that case, the Larson ratio is high and Leroy ratio is not in the range 0.7–1.3. Increasing the total hardness to 20°F (calcium hardness = 17.24°F) enables increasing the total alkalinity to obtain the calco-carbonic equilibrium of water, which decreases the Larson ratio and increases the Leroy ratio. However, it is not possible to increase total hardness above 20°F to obtain a Larson ratio below 1, because water would then be too hard.

- $\text{CO}_2 + \text{CaCO}_3 + \text{Na}_2\text{CO}_3 + \text{Cl}_2$  (treatments 3–6)

This treatment also makes it possible to meet guidelines for chlorides and sodium. Chemical doses for treatments 3 and 5 are calculated for final calcium hardness of 8°F. The total alkalinity obtained is higher than the one obtained with the previous treatment,  $\text{CO}_2 + \text{Ca}(\text{OH})_2$ . The Larson ratio is lower and the Leroy ratio is higher and water is then slightly less corrosive. Treatments 3 and 5, 4 and 6, lead to the same final composition of water. As previously, an increase of total hardness up to 20°F decreases the Larson ratio and increases the Leroy ratio. The use of the dolomite form of calcium carbonate, as opposed to the calcite form, decreases  $\text{CO}_2$  consumption, but increases the calcium carbonate consumption.

- $\text{CaCl}_2 + \text{NaHCO}_3 + \text{Cl}_2$  (treatments 7 and 8)

This method uses chemicals containing chlorides and sodium, so attention should be paid

Table 6  
Results of different remineralization treatments on standard permeate

Treatments	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Chemicals	CO <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	CaCl <sub>2</sub>	CaCl <sub>2</sub>	CaCl <sub>2</sub>	CaCl <sub>2</sub>	CaCl <sub>2</sub>	CaCl <sub>2</sub>	CaCl <sub>2</sub>	CaCl <sub>2</sub>
Action	↑total CO <sub>2</sub>	↑total CO <sub>2</sub>	↑total CO <sub>2</sub>	↑total CO <sub>2</sub>	↑total CO <sub>2</sub>	↑total CO <sub>2</sub>	↑THCa	↑THCa	↑THCa	↑THCa	↑THCa	↑THCa	↑THCa	↑THCa
Dosage, mg/l	61.607	150.16	99.567	112.034	66.347	75.09	83.8	70	83.8	70	83.8	70	70	70
Chemicals	Ca(OH) <sub>2</sub>	Ca(OH) <sub>2</sub>	CaCO <sub>3</sub>	CaCO <sub>3</sub>	CaCO <sub>3</sub>	CaCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>
Action	↑THCa	↑THCa	↑TAC	↑THCa	↑TAC	↑TAC	↑TAC	↑TAC	↑TAC	↑TAC	↑TAC	↑TAC	↑TAC	↑TAC
Dosage, mg/l	55.87	124.265	105.933	117.809	139.16	154.761	365.009	403.033	14.429	14.926	150	100	150	194
Chemicals	—	—	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	—	—	—	—	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>
Action	—	—	Saturation at 1.2	Saturation at 1.2	Saturation at 1.2	Saturation at 1.2	—	—	—	—	↑TAC	↑TAC	↑TAC	↑TAC
Dosage, mg/l	—	—	5.933	6.302	5.933	6.302	—	—	—	—	10.851	12.573	11.323	9.937
Chemicals	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>
Dosage, mg/l	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
pH	8.3	7.63	7.99	7.91	7.99	7.91	7.87	7.9	9.18	9.24	8.19	8.41	8.26	8.17
TH, °F	10.757	20	18.307	20	18.307	20	10.757	9.514	10.757	9.154	10.757	9.514	9.514	9.514
THCa, °F	8	17.24	8	8.85	8	8.85	8	6.76	8	6.76	8	6.76	6.76	6.76
TAC, °F	7.375	16.618	15.485	17.213	15.485	17.213	21.552	23.815	1.187	1.233	9.752	6.964	9.822	12.31
Saturation index	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Na <sup>+</sup> , mg/l	119.2	119.2	121.775	121.935	121.775	121.935	219.143	229.554	125.462	125.677	164.863	152.037	165.185	176.631
Cl <sup>-</sup> , mg/l	204.8	204.8	204.8	204.8	204.8	204.8	258.402	249.575	258.402	249.575	258.402	249.575	249.575	249.575
Larson ratio	4.161	1.813	1.959	1.759	1.959	1.759	1.757	1.538	38.977	37.307	3.921	5.374	3.776	3
Leroy ratio	0.686	0.831	0.846	0.861	0.846	0.861	2.004	2.503	0.11	0.13	0.907	0.732	1.032	1.294
Conductivity, μS/cm	625.9	762.8	746.1	771.5	746.1	771.5	943.3	957.8	646.2	628.3	772.8	713.5	755.6	792
SAR	5	4	4	4	4	4	9	10	5	6	7	7	7	8

not to exceed the guidelines for these ions. The calcium hardness increase will be limited, as, for a value of 8°F, chlorides and sodium concentrations slightly exceed the guidelines. If calcium chloride concentration is lowered, in order not to exceed the guideline for chlorides, then the quantity of sodium bicarbonate to be added should increase to obtain an SI of 1.2. Then sodium concentration increases strongly. Thus, it will never be possible to respect, at the same time, guidelines for chlorides and sodium. The use of sodium bicarbonate strongly increases total alkalinity (21.552–23.815°F). This makes it possible to obtain a low Larson ratio. On the other hand, because of this high total alkalinity, Leroy ratio is important and exceeds the range 0.7–1.3.

- $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 + \text{Cl}_2$  (treatments 9 and 10)

As for treatments 7 and 8, chemicals containing chlorides and sodium are used, so, one should pay attention to respect guidelines for these ions. However, as the sodium carbonate dose is smaller than sodium bicarbonate dose in treatment 7, the guideline value for sodium is not exceeded, for the desired total hardness. The sodium carbonate dose being very low to reach equilibrium, the total alkalinity is very low for a given calcium hardness value. The Larson ratio is consequently high and the Leroy ratio is very low. Even for calcium hardness values less than 8°F, the Larson ratio will always be very high (see treatment 9). Finally, the pH obtained through this type of treatment is high and close to the prescribed limit. For all these reasons, it will not be possible to select this treatment.

- $\text{CaCl}_2 + \text{NaHCO}_3 + \text{Na}_2\text{CO}_3 + \text{Cl}_2$  (treatments 11–14)

This fifth solution has been considered, which would retain the positive aspects of the treatments using sodium carbonate and bicarbonate. As in the case of the treatments 7–10, it is not possible to reach 8°F value for calcium hardness, because

the added calcium chloride dose is such that chloride concentration guideline is exceeded (see treatment 11). Therefore, a lower value for calcium hardness should be obtained. Increasing quantities of sodium bicarbonate have been tested to check evolution of the various parameters, for a calcium hardness of 6.76°F. The following was noted: 1) Larson ratio decreases, 2) Leroy ratio increases. To maintain the Leroy ratio in the range 0.7–1.3, the  $\text{NaHCO}_3$  dosage should not exceed 194 mg/l.

#### 5.4. Treatments to be selected

The two main problems are:

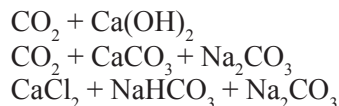
- Chlorides and sodium concentrations must not exceed guidelines. This problem is only faced when calcium chloride is used.
- Treated waters are more or less corrosive. The Larson ratio is always higher than 1, and Leroy ratio is not always in the range 0.7–1.3.

The optimized treatments giving the lowest values of Larson ratio are summarized below in increasing order of these values:

treatment 8 ( $\text{CaCl}_2 + \text{NaHCO}_3$ ) < treatment 7 ( $\text{CaCl}_2 + \text{NaHCO}_3$ ) < treatments 4 and 6 ( $\text{CO}_2 + \text{CaCO}_3$ ) < treatment 2 ( $\text{CO}_2 + \text{Ca(OH)}_2$ ) < treatment 14 ( $\text{CaCl}_2 + \text{NaHCO}_3 + \text{Na}_2\text{CO}_3$ )

Nevertheless, for treatments 7 and 8, guidelines limits for chlorides and sodium concentrations cannot be respected and the Leroy ratio cannot be kept in the range 0.7–1.3.

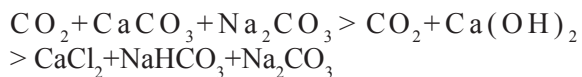
The selected treatments are, thus, as follows:



which makes it possible to obtain a low Larson ratio, to be in the good range for the Leroy ratio, and to respect guidelines for chlorides and sodium.

#### 5.5. Technico-economical considerations

From the investment point of view, the above three treatments are classified as follows:



Treatments using  $\text{CO}_2$  require local availability of the chemical. Moreover, storage of this gas means that the gas supplier provides the plant with a refrigerated tank (usually for rent). Calcium carbonate is most of the time not available locally. Filters of large dimensions (filtration rate about 10 m/h) should be provided and they must be refilled regularly. But operation of the unit is very simple, as the total alkalinity and calcium hardness to be reached only depend on  $\text{CO}_2$  dosage. Lime is available and cheap, but very difficult to prepare and dose (need for preparation of lime water in a saturator not to increase the turbidity of the treated water). Treatments combining three chemicals (calcium chloride, sodium bicarbonate, sodium

carbonate) only need standard equipment for preparation and dosing (stirred tanks and metering pumps). Moreover, total alkalinity and calcium hardness can be adjusted independently. Operation cost of the three methods can be compared, using a basis of 100 for the cost of lime. From Table 7, the less expensive treatment regarding operation is  $\text{CO}_2 + \text{Ca(OH)}_2$ .

To conclude with, remineralization treatments can be chosen on the basis of different parameters, as shown in Table 8.

## 6. The influence of required treated water quality on design and operation of SWRO plants

The study of the post-treatment to be applied to a standard permeate (average salinity and tem-

Table 7  
Operation cost comparison of selected treatments

Chemical	Chemical price 100%	Dosage, g/m <sup>3</sup>	Cost for 1000 m <sup>3</sup>
Treatment: $\text{CO}_2 + \text{Ca(OH)}_2$			
$\text{CO}_2$	370	150.16	55.56
$\text{Ca(OH)}_2$	100	124.265	12.43
Total cost			67.99
Treatment: $\text{CO}_2 + \text{CaCO}_3 + \text{Na}_2\text{CO}_3$			
$\text{CO}_2$	370	112.034	41.45
$\text{CaCO}_3$	425	117.809	50.07
$\text{Na}_2\text{CO}_3$	260	6.302	1.64
Total cost			93.16
Treatment $\text{CaCl}_2 + \text{NaHCO}_3 + \text{Na}_2\text{CO}_3$			
$\text{CaCl}_2$	380	70	26.6
$\text{NaHCO}_3$	230	194	44.62
$\text{Na}_2\text{CO}_3$	260	9.937	2.58
Total cost			73.80

Table 8  
Choices of permeate treatments regarding different criteria

Criteria of choice	$\text{CO}_2 + \text{Ca(OH)}_2$	$\text{CO}_2 + \text{CaCO}_3 + \text{Na}_2\text{CO}_3$	$\text{CaCl}_2 + \text{NaHCO}_3 + \text{Na}_2\text{CO}_3$
Investment	2	3	1
Operation cost	1	3	2
Quality of treated water	2	1	3
Operating easiness	3	1	2

perature) allows us to focus on several important parameters:

- High concentrations for chlorides and sodium, that give water corrosive properties which cannot be completely reduced by remineralization
- Boron concentration, which almost reaches guideline values for drinking water.

Regarding the above three parameters (chlorides, sodium, boron) the conclusions would be even more severe if:

- seawater mineralization
- temperature
- recovery

were higher than the standards taken into account for this study.

To deal with this deterioration, one would modify the plant design as follows:

- by using membranes with higher rejection, especially regarding boron
- by reducing the recovery
- by increasing the feed pressure
- by increasing pH of raw water to increase the retention of boron

And finally, we foresee a second pass of permeate on membranes used for brackish water (BWRO), the two permeates being then mixed. This last solution is the only one that guarantees, with ad hoc post-treatments, a final treated water neither aggressive (calco-carbonic equilibrium), nor corrosive (related to chlorides content). Fig. 4 shows such a process.

When operating the plant, seawater temperature may change. Its decrease will increase permeate quality. On the other hand, an increase of temperature will increase passage of salts. In that case, in order to maintain permeate quality, the active surface of membranes should be reduced by shutting down some of the pressure vessels.

### 7. Conclusions

When designing and operating the plants, great attention should be paid to the quality of the permeate at the outlet of SWRO plants, in order to limit corrosion of pipes and equipment and to meet drinking water standards. In particular, post-treatments must be properly studied, especially when using single pass RO units, taking into

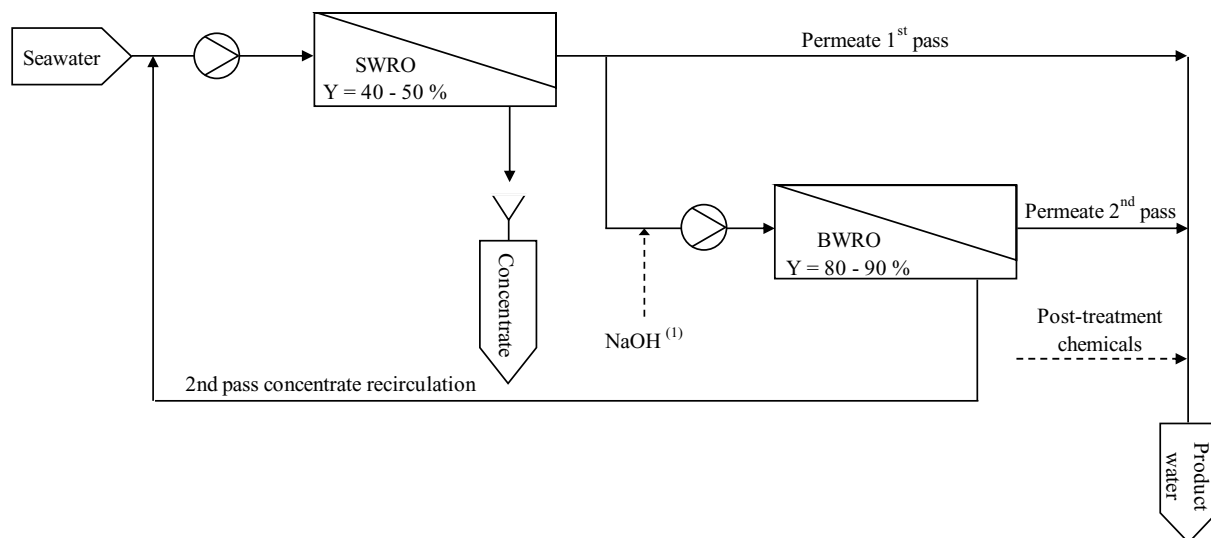


Fig. 4. Process flow-sheet for a double-pass system.

account local conditions (availability and price of chemicals), and investment budget allocated to the projects. Furthermore, when establishing the permeate quality, one should not only take into account the data obtained through membranes manufacturers' software. It is necessary to obtain guarantees on the real permeate chemical quality versus time (ageing of membranes) according to the projected membrane replacement planning. A safety allowance will take into account possible variations of seawater composition and ageing of membranes.

## References

- [1] American Water Works Association, *Water Quality and Treatment*, 5th ed., 1999.
- [2] L. Legrand and P. Leroy, *Prévention de la corrosion et de l'entartrage dans les réseaux de distribution d'eau*, 1995.
- [3] American Water Works Association, *Reverse Osmosis and Nanofiltration*, 1st ed., 1999.
- [4] Hydranautics, *Evaluation of Boron Reduction Processes in RO Seawater Systems*, 2002.
- [5] World Health Organization, *Guidelines for Drinking Water Quality, Recommendation*, 2nd ed., vol. 1, 1993 and addendum to vol. 1, 1998.
- [6] N. Morin, *The Quality of Irrigation Water: a Factor not to Be Overlooked*, [www.asgq.org](http://www.asgq.org).
- [7] *Qualité des eaux destinées à la consommation humaine*, Directive européenne 98/83/CE du conseil du 3 Novembre 1998.