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

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## Abstract

Permeate quality of SWRO plants is suitable neither for drinking water nor for irrigation purpose : treatments must be adjusted to decrease boron concentration and post-treatments are required to improve water mineralization in order to correct its corrosiveness tendency.
Several chemical strategies were studied and the evolution of different indicators were analyzed to evaluate the quality of the product water before distribution, among which Leroy and Larson ratios. Corrosive quality of the permeate remains the critical factor because of its high chloride concentration. Different strategies can be used to produce drinking water or irrigation water from sea water: chemicals addition 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* : sea water; 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 sea water reverse osmosis (SWRO) desalination plants and this is easily understandable. On the opposite, 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.

We will talk, here, about sea water desalination plants designed for the production of drinking water, and its additionnal uses for private or public garden watering. We will not cover post-treatments required for the production of industrial waters, because of its specific end-uses (process, cooling circuits, boilers feed…) which generaly dictate point of use treatments .

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

## 2. CHARACTERISTICS OF PERMEATE

Mediterranean sea water 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 sea water, which will be the standard for this study, and acidified seawater entering membranes (sulphuric acid is used).

Elements such as baryum, strontium, fluorides, bromides, silica have been neglected because of their low concentration in sea water and consequently in the permeate.

| CATIONS (mg/l AS ION) | NON ACIDIFIED FEED | ACIDIFIED FEED | ANIONS (mg/l AS ION) | NON ACIDIFIED FEED | ACIDIFIED FEED |
|---|---|---|---|---|---|
| $Ca^{2+}$ | 450,00 | 450,00 | $HCO_3^-$ | 153,00 | 127,80 |
| $Mg^{2+}$ | 1 410,00 | 1 410,00 | $SO_4^{2-}$ | 2 700,00 | 2 721,20 |
| $Na^+$ | 11 849,00 | 11 849,00 | $Cl^-$ | 21 500,00 | 21 500,00 |
| $K^+$ | 440,00 | 440,00 | | | |
| Total boron : 5,5 mg/l<br>pH : 8,10 (7,00 for acidified feed)<br>Free $CO_2$ : 2,90 mg/l (21,90 mg/l for acidified feed)<br>TDS : 38 502,00 mg/l (38 498,00 mg/l for acidified feed) | | | | | |

*Table 1: Characteristics of reference seawater, before and after acidification*

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 %

| CATIONS | mg/l AS ION | | ANIONS | mg/l AS ION | |
|---|---|---|---|---|---|
| | NON ACIDIFIED FEED | ACIDIFIED FEED | | NON ACIDIFIED FEED | ACIDIFIED FEED |
| $Ca^{2+}$ | 1,80 | 1,80 | $HCO_3^-$ | 2,30 | 1,90 |
| $Mg^{2+}$ | 6,70 | 6,70 | $SO_4^{2-}$ | 10,90 | 11,00 |
| $Na^+$ | 119,20 | 119,20 | $Cl^-$ | 203,30 | 203,50 |
| $K^+$ | 6,60 | 6,60 | | | |
| | NON ACIDIFIED FEED | | | ACIDIFIED FEED | |
| Total boron | 0,44 mg/l | | | 0,55 mg/l | |
| pH | 5,57 | | | 4,95 | |
| Free $CO_2$ | 2,90 mg/l | | | 21,90 mg/l | |
| TDS | 350,80 mg/l | | | 350,70 mg/l | |

*Table2: Permeate analysis obtained from reference sea water*

As the cut-off point of RO membranes is very low (< 0,001 µm) water is perfectly disinfected.

Permeate contains over 92% of sodium chloride, which is the main characteristic of a permeate produced from sea water.

As for boron, the WHO guideline is still respected if raw water is not acidified. In that case, particular attention should be payed to chemical pre-treatment in order to avoid calcium carbonate and magnesium hydroxyde precipitation on membranes : sulfuric acid must be replaced by a scale inhibitor.

## 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 §2, attention is paid to sodium and chlorides.

Table 3 gives standards from European Union (Directive 98/83/CE of November the 3rd of 1998) and World Health Organization (WHO).

| | EUROPEAN STANDARD | WHO [1] |
|---|---|---|
| Chlorides | 250 mg/l | 250 mg/l [2] |
| Sulfates | 250 mg/l | 250 mg/l |
| Sodium | 200 mg/l | 200 mg/l [3] |
| Boron | 1 mg/l | 0,5 mg/ [4] |
| Conductivity | 2 500 µS/cm | - |
| TDS | - | < 600 mg/l : good palatability [5]<br>> 1 200 mg/l : unpalatable [5] |
| pH | 6,5 à 9,5 | - |
| [1] Levels likely to give rise to consumer complains or guideline value for Boron | | |
| [2] Reasons for consumer complains : taste, corrosion | | |
| [3] Reasons for consumer complains : taste | | |
| [4] Provisional guideline value – Available information on health effects is limited | | |
| [5] Guideline value, which is not health – based, has been proposed | | |

*Table 3: Required and recommended values from European Union and WHO*

## 3.2 QUALITY FOR NETWORKS AND EQUIPMENTS PROTECTION AGAINST CORROSION

### 3.2.1 Calco-carbonic balance

Various chemical compounds are dissolved in naturel water. The main element is calcium carbonate which equilibrium depends on interactions with $CO_2$.

Figure 1 gives different forms of $CO_2$ in water. Chemical equilibrium linked to calcium carbonate, called "calco-carbonic balance", can be shifted under $CO_2$ action : calcium carbonate can be either dissolved (aggressive water) or precipitated (scale forming water).

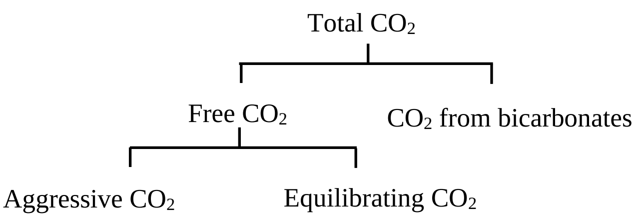



*Figure 1: Distribution of different $CO_2$ forms in water*

Water at equilibrium neither dissolves, nor precipitates calcium carbonate : it is then characterised by its saturation pH, called pHs.
The Hoover Nomogram presented in figure 2 enables to determine pHs for water .

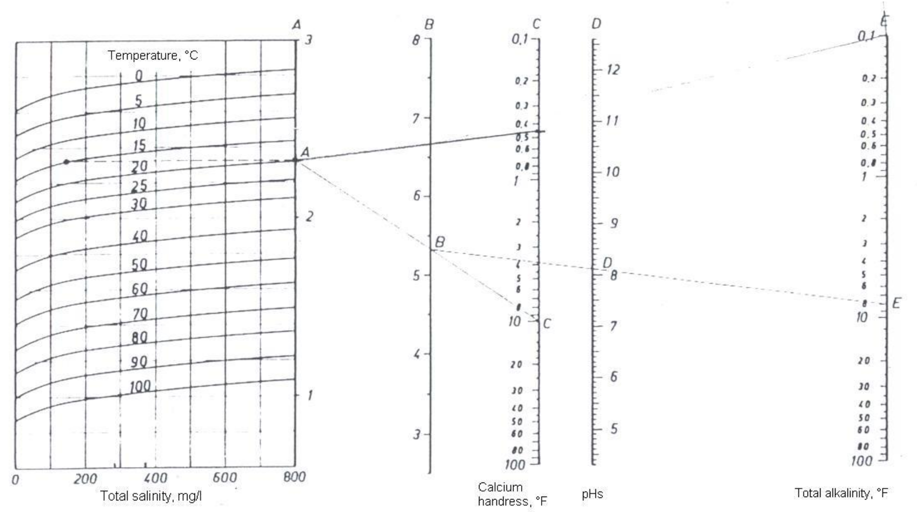


*Figure 2: Hoover Nomogram for saturation pH determination*

It is also possible, using various calculations, to determine if water is aggressive, scale forming or corrosive, thanks to following ratios :

- Langelier index (LI),
- Ryznar index (RI),
- Larson ratio (LnR),
- Leroy ratio (LyR),
- saturation index (SI).

In order to protect distribution networks and equipments, 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 – pHs

If LI<0, water is aggressive
If LI >0, water is scale forming

Ryznar Index

RI = 2pHs – pH.

It quantitatively defines the aggresiveness or the scaling potential of aerated water.
Water with pHs of 7 is scalant if RI is less than 7 and aggressive if RI is more than 7.

Saturation Index

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

where : K's = solubility product of calcium carbonate,
$Ca^{2+}$ and $CO_3^{2-}$, 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, Saturation Index will be used for the rest of the study, as it is the most accurate index.

Indeed, 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 chlorides 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 chlorides and/or sulfates ions.

This empiric formula is based on many experiments performed by Larson and Skold, who estimated that it should not exceed 0.2 to 0.3. Other authors assessed that values up to 1 were acceptable.

| LR | CORROSIVE POTENTIAL |
|---|---|
| < 0,2 | no potential |
| 0,2 to 0,4 | small potential |
| 0,4 to 0,5 | slight potential |
| 0,5 to 1 | average potential |
| > 1 | strong potential |

*Table 5: Corrosive potential of water regarding Larson ratio values*

Leroy Ratio

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

Total alcalinity 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 criterias are essential for this application : mineralisation, sodium and boron concentrations.

Total mineralisation 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 SAR (Sodium Adsorption Ratio), takes into account mutual effects of these three ions :

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

Na, Ca and Mg in méq/l.

| SAR | EFFECTS OF SODIUM |
|---|---|
| ≤ 10 | No effects – suitable for every kind of soil |
| 10,1 à 18 | Risks of accumulation in case of fine soils – suitable for sandy soils |
| 18,1 à 26 | Risks for every kind of soils – need to use a conditioner and to improve drainage |
| > 26,1 | Water not suitable for irrigation |

*Table 6: Effects of sodium on soils depending on SAR value*

For fruit trees, boron is toxic when its concentration is above 1 mg/l. A concentration of 0,5 mg/l approximatively is necessary to avoid marks on fruit, which would deteriorate their appearance.

## 4. CORRECTIVE ACTIONS ON PERMEATE

### 4.1 CORRECTIONS FOR DRINKING WATER PURPOSE

Althought reverse osmosis eliminates bacterias and viruses, chlorine must be added to water so that its remanent 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 almost represent 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 ionisation of boric acid and improves its rejection by membranes. Figure 3 gives an idea of membranes rejection of boron species as a function of the pH, for sea water.

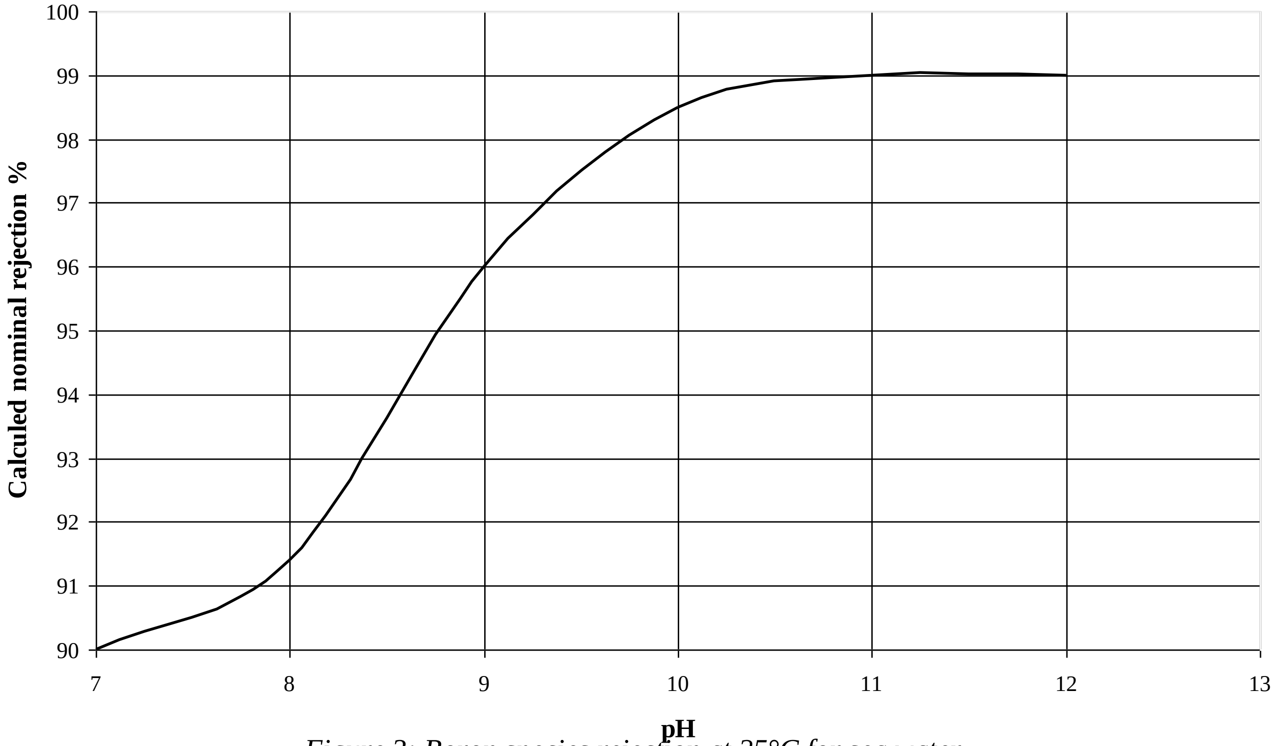


*Figure 3: Boron species rejection at 25°C for sea water*

## 4.2 CORRECTIONS FOR PROTECTION AGAINST CORROSION

As explained before, the corrosive potential of water is characterised by two indexes: Larson Ratio and Leroy Ratio.
For no corrosion risk, LnR should be less than 1 and LyR should be between 0.7 and 1.3. This means that either chlorides and sulfates concentrations should be low, and bicarbonates concentration should be important.

At the outlet of the reverse osmosis units, water is very corrosive. Indeed, the chlorides concentration is very important and other ions concentrations are very low (except sodium). As it is not easy to decrease the chlorides concentration, the total alkalinity should be increased. This will lower Larson Ratio and give the Leroy Ratio in the required range.

As we will see later, the optimum Larson's 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 pipes and equipments internal surfaces. 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 ON THE POST-TREATMENTS TO BE CONSIDERED

In addition to chlorination, remineralization of the permeate is essential, mainely because of its corrosive properties. Moreover this remineralization improves the taste of water and its possibility of being used for irrigation.
Membranes feed water will not be acidified in order to fit with boron guideline given by European Union and WHO.

## 5. REMINERALIZATION TREATMENTS TO BE CONSIDERED

### 5.1 GENERALS

The different remineralization processes are :

- either by filtration on calcium carbonate, in calcite form ($CaCO_3$, MgO) or dolomite form ($CaCO_3$, $MgCO_3$), combined with carbone dioxide injection ($CO_2$). This treatment enables to obtain water at calco-carbonic balance, sodium carbonate $Na_2CO_3$ is injected then to increase the saturation index up to 1.2.

- or by chemicals injection: sodium carbonate ($Na_2CO_3$), sodium bicarbonate ($NaHCO_3$), calcium chloride ($CaCl_2$), lime ($Ca(OH)_2$), carbon dioxide ($CO_2$).

Calcium sulphate ($CaSO_4$) will not be discussed here. This chemical allows to increase the calcium hardness of water without increasing the chloride concentration. But using this product is difficult because of its low solubility (approx. 1.8 g/l at 20°C).

$CO_2$ stripping is not discussed neither, because:
- if the feed water is not acidified, free $CO_2$ concentration is very low and therefore difficult to eliminate by stripping,
- $CO_2$ can contribute to remineralization of water by bicarbonate formation,
- $CO_2$ 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 $CO_2$ : 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, $CO_2$,
- lime, $Ca(OH)_2$,
- sodium bicarbonate, $NaHCO_3$,
- sodium carbonate, $Na_2CO_3$,
- calcium chloride, $CaCl_2$,

with the following combinations:

- $CO_2 + Ca(OH)_2 + Cl_2$

- $CO_2 + CaCO_3 + Na_2CO_3 + Cl_2$
- $CaCl_2 + NaHCO_3 + Cl_2$
- $CaCl_2 + Na_2CO_3 + Cl_2$
- $CaCl_2 + NaHCO_3 + Na_2CO_3 + Cl_2$

Each treatement has been optimised 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 ($Na^+$, $Cl^-$ concentrations, index …), chemical dosages has been modified in order to correct it.

See table 7 hereafter for results:

| Treatments | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Chemicals** | **$CO_2$** | **$CO_2$** | **$CO_2$** | **$CO_2$** | **$CO_2$** | **$CO_2$** | **$CaCl_2$** | **$CaCl_2$** | **$CaCl_2$** | **$CaCl_2$** | **$CaCl_2$** | **$CaCl_2$** | **$CaCl_2$** | **$CaCl_2$** |
| **Action** | ↑ total $CO_2$ | ↑ total $CO_2$ | ↑ total $CO_2$ | ↑ total $CO_2$ | ↑ total $CO_2$ | ↑ total $CO_2$ | ↑ 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** | **$Ca(OH)_2$** | **$Ca(OH)_2$** | **$CaCO_3$, MgO** | **$CaCO_3$, MgO** | **$CaCO_3$, $MgCO_3$** | **$CaCO_3$, $MgCO_3$** | **$NaHCO_3$** | **$NaHCO_3$** | **$Na_2CO_3$** | **$Na_2CO_3$** | **NaHCO3** | **NaHCO3** | **NaHCO3** | **NaHCO3** |
| **Action** | ↑ THCa, ↑ TAC | ↑ THCa, ↑ TAC | ↑ TAC, ↑ THCa | ↑ TAC, ↑ THCa | ↑ TAC, ↑ THCa | ↑ TAC, ↑ THCa | ↑ 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** | - | - | **$Na_2CO_3$** | **$Na_2CO_3$** | **$Na_2CO_3$** | **$Na_2CO_3$** | - | - | - | - | **$Na_2CO_3$** | **$Na_2CO_3$** | **$Na_2CO_3$** | **$Na_2CO_3$** |
| **Action** | - | - | Saturatio at 1,2 | Saturatio at 1,2 | Saturatio at 1,2 | Saturatio 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** | **$Cl_2$** | **$Cl_2$** | **$Cl_2$** | **$Cl_2$** | **$Cl_2$** | **$Cl_2$** | **$Cl_2$** | **$Cl_2$** | **$Cl_2$** | **$Cl_2$** | **$Cl_2$** | **$Cl_2$** | **$Cl_2$** | **$Cl_2$** |
| **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 |
| **$Na^+$ (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 |
| **$Cl^-$ (mg/L)** | 204,8 | 204,8 | 204,8 | 204,8 | 204,8 | 204,8 | 258,402 | 249,575 | 258,402 | 249,575 | 128,402 | 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 |
| **Total Dissolved Solids (mg/L)** | 470 | 620 | 589 | 616 | 589 | 616 | 796 | 820 | 453 | 440 | 597 | 537 | 585 | 626 |

*Table 7: Results of different remineralization treatments on standard permeate*

## 5.3 COMMENTS ON THE RESULTS OBTAINED THROUGH VARIOUS REMINERALISATION TREATMENTS

**Preliminary remark :**

Several conclusions can be made. Whatever the treatment, a SI of 1.2 is always achieved, without excessive dosage of chemicals.
SAR values are always less than or equal to 10, and water obtained could be then used for every kind of soil.

**$CO_2$ + $Ca(OH)_2$ + $Cl_2$ (treatments 1 and 2)**

Carbon dioxide and lime addition 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, 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 to increase the total alkalinity to obtain the calco-carbonic equilibrium of water, which decreases Larson Ratio and increases 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.

**$CO_2$ + $CaCO_3$ + $Na_2CO_3$+ $Cl_2$ (treatments 3, 4, 5 and 6)**

This treatment also enables not to exceed guidelines for chlorides and sodium.

Chemicals 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, $CO_2$+$Ca(OH)_2$. Larson Ratio is lower and Leroy Ratio is higher, 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 enables to decrease the Larson Ratio and to increase the Leroy Ratio.

The use of dolomite form of calcium carbonate, as opposed to the calcite form, decreases $CO_2$ consumption but increases the calcium carbonate consumption.

**$CaCl_2$ + $NaHCO_3$ + $Cl_2$ (treatments 7 and 8)**

This method uses chemicals containing chlorides and sodium, so attention should be paid 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 guideline for chlorides, then, the quantity of sodium bicarbonate to be added should increase to obtain a SI of 1.2. Then sodium concentration increases strongly. So, 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°F to 23,815°F). This enables 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.

**$CaCl_2$ + $Na_2CO_3$ + $Cl_2$ (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 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. Larson Ratio is consequently high and Leroy Ratio is very low.

Even for calcium hardness values less than 8°F, 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.

**$CaCl_2$ + $NaHCO_3$ + $Na_2CO_3$ + $Cl_2$ (treatments 11, 12, 13 and 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 to 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 :

- Larson Ratio decreases,
- Leroy Ratio increases.

To maintain the Leroy Ratio in the range 0.7 – 1.3, the $NaHCO_3$ dosage shouldn't 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 precised below, in increasing order of these values :

Treatment 8 ($CaCl_2$ + $NaHCO_3$) < Treatment 7 ($CaCl_2$ + $NaHCO_3$) < Treatment 4 and 6 ($CO_2$ + $CaCO_3$) < Treatment 2 ($CO_2$ + $Ca(OH)_2$) < Treatment 14 ($CaCl_2$ + $NaHCO_3$ + $Na_2CO_3$)

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

The selected treatments are, thus, as follows :

- $CO_2 + Ca(OH)_2$,
- $CO_2 + CaCO_3 + Na_2CO_3$,
- $CaCl_2 + NaHCO_3 + Na_2CO_3$,

which enable to obtain a low Larson Ratio, to be in the good range for Leroy Ratio, and to respect guidelines for chlorides and sodium.

## 5.5 TECHNICO-ÉCONOMICAL CONSIDÉRATIONS

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

$$CO_2 + CaCO_3 + Na_2CO_3 > CO_2 + Ca(OH)_2 > CaCl_2 + NaHCO_3 + Na_2CO_3$$

Treatments using $CO_2$ require local availability of the chemical. Moreover, storage of this gas means that the gas supplier provides the plant with 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 $CO_2$ 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 equipments 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, on the basis 100 for the cost of lime (100%). From table 8 hereafter, the less expensive treatment regarding operation is $CO_2 + Ca(OH)_2$.

| **CHEMICAL** | **CHEMICAL PRICE 100%** | **DOSAGE g/m$^3$** | **COST FOR 1 000 m$^3$** |
|---|---|---|---|
| ***Treatment: $CO_2 + Ca(OH)_2$*** | | | |
| $CO_2$ | 370 | 150.16 | 55.56 |
| $Ca(OH)_2$ | 100 | 124.265 | 12.43 |
| Total cost | | | 67.99 |
| ***Treatment: $CO_2 + CaCO_3 + Na_2CO_3$*** | | | |
| $CO_2$ | 370 | 112.034 | 41.45 |
| $CaCO_3$ | 425 | 117.809 | 50.07 |
| $Na_2CO_3$ | 260 | 6.302 | 1.64 |
| Total cost | | | 93.16 |
| ***Treatment $CaCl_2 + NaHCO_3 + Na_2CO_3$*** | | | |
| $CaCl_2$ | 380 | 70 | 26.6 |
| $NaHCO_3$ | 230 | 194 | 44.62 |
| $Na_2CO_3$ | 260 | 9.937 | 2.58 |
| Total cost | | | 73.80 |

*Table 8: Operation cost comparison of selected treatments*

To conclude with, remineralization treatments can be chosen on the basis of different parameters, as shown in table 9.

| **Criteria of choice** | **$CO_2 + Ca(OH)_2$** | **$CO_2 + CaCO_3 + Na_2CO_3$** | **$CaCl_2 + NaHCO_3 + Na_2CO_3$** |
|---|---|---|---|
| Investment | 2 | 3 | 1 |
| Operation cost | 1 | 3 | 2 |
| Quality of treated water | 2 | 1 | 3 |
| Operating easiness | 3 | 1 | 2 |

*Table 9: Choices of permeate treatments regarding different criteria*

## 6. <u>**THE INFLUENCE OF REQUIRED TREATED WATER QUALITY ON DESIGN AND OPERATION OF SWRO PLANTS**</u>

The study of the post-treatment to be applied to a standard permeate (average salinity and temperature) enables 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 :

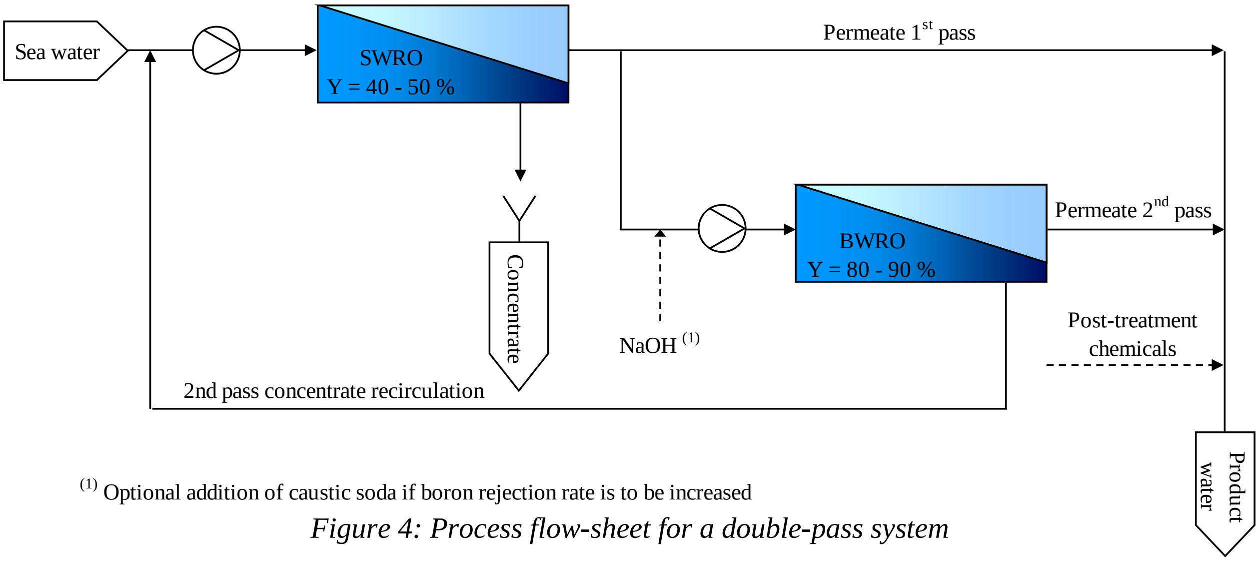
. seawater mineralization,
. temperature,
. recovery,

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 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).
Figure 4 shows such a process.




(1) Optional addition of caustic soda if boron rejection rate is to be increased

*Figure 4: Process flow-sheet for a double-pass system*

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

## 7. CONCLUSIONS

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 equipments,
- meet drinking water standards,

and this, when designing and operating the plants.

In particular, post-treatments must be properly studied, especially when using a single pass RO units, taking into account local conditions (availability and price of chemicals), and investment costs allocated to the projects.

Furthermore, when establishing the permeate quality, one should not only take into account the data obtained through membranes manufacturers' sofware. It is necessary to obtain guarantees on the real permeate chemical quality versus time (ageing of membranes) according to the projected membranes replacement planning.

A safety allowance will take into account possible variations of seawater composition and ageing of membranes.

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