

## Optimal levels of remineralisation for desalinated waters

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### ABSTRACT

The purpose of remineralization is generally to produce water with a Langelier saturation index (LSI) very close to zero that remains stable in contact with the atmosphere. It is also important to accomplish this with the lowest possible consumption of CO<sub>2</sub> to minimize operating costs. This study considers the way to adequately remineralize desalinated water for a range of temperatures of between 14°C and 25°C. At most desalination plants, CO<sub>2</sub> needs to be added following reverse osmosis and prior to remineralization. The concentration of CO<sub>2</sub> in osmotized water required to reach the proposed levels of remineralization depends on the permeate alkalinity prior to remineralization. In this article, the dosage is shown that is required for each water according to the pH and alkalinity of the permeate prior to remineralization with calcite beds. In the case of using Ca(OH)<sub>2</sub>, the dosage of CO<sub>2</sub> should be doubled. Underdosing of CO<sub>2</sub> produces water with low alkalinity. This implies a low buffering capacity and, therefore, a tendency to easily acidify through uptake of CO<sub>2</sub> from the atmosphere. This fact, coupled with the low calcium content, makes this type of water unstable, with a tendency to be corrosive. Overdosing of CO<sub>2</sub> implies higher alkalinity and hardness in remineralized water, as well as a CO<sub>2</sub> content that tends to decrease in contact with the atmosphere, causing the pH of the water to increase and thus giving rise to a slightly positive LSI. It is noted that the hardness of the remineralized water does not usually reach 100 mg CaCO<sub>3</sub>, while the LSI is between 0.5 and 1.0, even at temperatures of 40°C. In many water distributions networks LSI values of between +0.1 to +0.5 are required to protect the facilities. This is achieved in the case of CaCO<sub>3</sub> post-treatment by slightly increasing the pH through the addition of NaOH (2–4 mg NaOH/L). In Ca(OH)<sub>2</sub> facilities this is done with a slight overdose of Ca(OH)<sub>2</sub>. On some occasions, technical limitations in controlling the exact dose of Ca(OH)<sub>2</sub> may cause an increase in turbidity above 1 NTU.

*Keywords:* Remineralisation; Desalinated water; Temperature, CO<sub>2</sub>; pH; Langelier saturation index

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### 1. Introduction

Remineralisation is understood as the set of techniques that manage to increase the hardness and alkalinity of water to values that provide a saturation index, also called the Langelier saturation index (LSI), equal to or close to zero and in balance with the atmosphere. The CO<sub>2</sub> concentration of a water in equilibrium with the CO<sub>2</sub> in the atmosphere naturally defines the pH and the combination

of carbonates and bicarbonates that corresponds to this pH. In open systems, when the CO<sub>2</sub> content of the water is higher than it should be in equilibrium with the air, the CO<sub>2</sub> escapes from the atmosphere and the pH increases. Conversely, if the CO<sub>2</sub> content is lower than it should be in equilibrium with the atmosphere, the water will absorb CO<sub>2</sub> from the atmosphere and the pH will decrease. The aim of remineralization is, on the one hand, to reach the carbon dioxide equilibrium point [1,2], where the pH,

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dissolved calcium and alkalinity do not vary or vary very little in contact with the atmosphere, and, on the other, to do so as accurately as possible to minimise the consumption of energy and chemical products, especially  $\text{CO}_2$ . The process of balancing  $\text{CO}_2$  with the atmosphere depends on the temperature and partial pressure of  $\text{CO}_2$  [3–6].

However, in the operating conditions of desalination plants only the water temperature can vary significantly. These differences are only seasonal and do not occur in short periods during the remineralization operation. In this article, the first task is to analyse the behaviour of different remineralized waters to check the concentration of  $\text{CO}_2$  in equilibrium with the atmosphere and in the conditions of the Mediterranean coast. Next, the evolution of the saturation pH (pHsat), the equilibrium pH (pHeq) and the pH of the water at different levels of remineralization is analysed using a mathematical model. The objective is to identify the optimum level of remineralization that produces an LSI very close to zero and with a  $\text{CO}_2$  content in equilibrium with that of the atmosphere. The relationship between the  $\text{CO}_2$  content and the pH of the water is also evaluated based on the data obtained. Finally, data are presented on the evolution of the pH, bicarbonates, and LSI of the remineralized water and water in contact with the atmosphere, to corroborate the theoretical analysis of the first part of the article and help define the optimum levels of remineralization [1,7,8].

## 2. Material and methods

To analyse the behavior of the remineralized water in equilibrium with the atmosphere, samples were taken from different desalination plants after the remineralization treatment and *in situ* analyses were carried out of pH, electrical conductivity, temperature, bicarbonates, and carbonates. The sample was subsequently exposed to the atmosphere and gently stirred mechanically, taking samples for analysis every few days for up to 14 d.

The LSI is calculated from the values of electrical conductivity or total dissolved solids, calcium, alkalinity, pH and temperature. In practice, the conductivity, pH and temperature are calculated. In most desalination plants, calcium is measured continuously, but it requires a specific and more expensive probe [9–12].

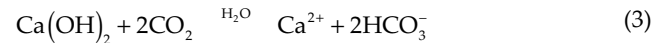
The LSI of the remineralized water can be calculated from the increase in electrical conductivity produced by the remineralization using the quotient:

$$\frac{\Delta \text{CE}}{\Delta \text{Alk}} = 2.976 \text{E-}7 \times [\text{CE}_{25(\text{o})}]^2 - 0.0006 \times \text{CE}_{25(\text{o})} + 1.84 \quad (1)$$

The calcium value of the remineralized water is estimated as  $\text{Ca}^{2+}(\text{r}) = \text{Alk}(\text{r})/2.5$ . The pH used is the pH measured *in situ*, along with that corresponding to temperature [1,9–12].

Once all the parameters have been obtained, the LSI can be calculated. It allows to estimate the LSI in between +0.5 and –0.5. The LSI approaches the concept of saturation using pH as a main variable. The LSI can be interpreted as the pH change required to bring water to equilibrium. Water with an LSI of 1.0 is one pH unit above saturation [9–12].

The pHeq corresponds to the pH of the acid–base chemical equilibrium of reaction:



It is evident from these reactions that the increase in electrical conductivity produced by remineralization is directly proportional to the increase in alkalinity, since only the calcium and bicarbonate content have increased.

In processes in which hydrochloric or sulfuric acid is added instead of  $\text{CO}_2$  the proportions are different; however, these cases are not considered in this paper.

The pHeq is obtained from analysis of the acid–base chemistry and in accordance with the Henderson–Hasselbach formula [1,4]. Consequently, pHeq does not depend on whether the solution is saturated with calcite.

When the solution is saturated with calcite and is at the acid–base equilibrium pH, pHeq coincides with pHsat and the LSI is equal to zero. Figs. 3–5 illustrate the difference between pHeq and pHsat.

With respect to the indirect calculation of LSI based on electrical conductivity at 25°C ( $\text{EC}_{25}$ ) and pH data prior to and following remineralization (depending on the permeate  $\text{EC}_{25}$ ):

$$\frac{\Delta \text{EC}_{25}}{\Delta \text{Alk}} = 1.55 - 1.75 \quad (4)$$

where:

$$\Delta \text{Alk} = \text{Alk}(r) - \text{Alk}(0) \quad (5)$$

and

$$\Delta \text{EC}_{25} = \text{EC}_{25}(r) - \text{EC}_{25}(0) \quad (6)$$

Consequently, and in view of the above, investigation of the relationship between the increase of  $\Delta \text{EC}_{25}$  and  $\Delta \text{Alk}$  is justified to be able to extrapolate the alkalinity values of remineralized water.

For instance,  $\text{Alk}(0)$  ranges from 0.5 to 2.8 mg  $\text{CaCO}_3/\text{L}$  for  $\text{EC}_{25}(0)$  values between 250  $\mu\text{S}/\text{cm}$  and 700  $\mu\text{S}/\text{cm}$ , respectively. The  $\text{Ca}(r)$  value of remineralized water can be calculated from the ratio  $\text{Ca}(r) = \text{Alk}(r)/2.5$ . The  $\text{pH}(r)$  and  $T(r)$  values will be those acquired *in situ* with the measuring equipment placed in line. Once all the parameters have been obtained, the  $\text{LSI}(r)$  calculation method should be the SM-2330 [11].

As in the case of desalinated water, a good relationship with the Tillmans formula (7) is confirmed:

$$\text{pH}_E = 7 - \log \frac{3[\text{CO}_{2\text{free}}]}{0.61[\text{Alk}]_{\text{at } 17^\circ\text{C}}} \quad (7)$$

This relationship corresponds practically to the formula presented by Tillmans and published in 1912 [1,3], where the concentrations of  $\text{CO}_2$  and alkalinity are expressed in mg/L. Fig. 15 shows the clear relationship between both parameters.

The different remineralization techniques, equations, and methods are shown in Table 1. The most widely used of these 5 remineralization techniques are numbers 1 and 2. Further information on these methods can be found in the literature [9–12].

Total hardness is defined as the sum of concentrations of calcium and magnesium in accordance with the formula:

$$\frac{\text{mgCaCO}_3}{\text{L}} = 2.497[\text{Ca}^{2+}, \text{mg/L}] + 4.118[\text{Mg}^{2+}, \text{mg/L}] \quad (8)$$

When milligrams of CaCO<sub>3</sub> of hardness exceed the milligrams of CaCO<sub>3</sub> of alkalinity, the milligrams of CaCO<sub>3</sub> defined by alkalinity are understood to refer to carbonated hardness and the rest to non-carbonated hardness. The total hardness of desalinated and remineralized waters is greater than the alkalinity. It is understood that, in this case, the non-carbonated Ca and Mg is combined with chloride and sulphate anions [9–12].

### 2.1. Simplified method for the calculation of pHsat

In respond to the demand for a numerical procedure for the calculation of pHsat, and in accordance with the work of Larson and Buswell [1] which follows Eq. (9), a simplified formula has been developed for the calculation of pHsat (13), which is becoming widespread because of its simplicity.

$$\text{LaI} = \frac{([\text{Cl}^-] + [\text{SO}_4^{2-}])}{([\text{HCO}_3^-] + [\text{CO}_3^{2-}])} \quad (9)$$

where the assessment criteria are as follows:

$$\text{LaI} > 1.2 \quad \text{High degree of corrosion} \quad (10)$$

$$0.8 < \text{LaI} < 1.2 \quad \text{Significant degree of corrosion} \quad (11)$$

$$\text{LaI} < 0.8 \quad \text{No risk of corrosion} \quad (12)$$

$$\text{pH sat} = (9.3 + A + B) - (C + D) \quad (13)$$

where:

$$A = 1 / 10(\log(\text{TDS}) - 1) \quad (14)$$

$$B = -13.2 \times \log(T(^{\circ}\text{C}) + 273.2) + 34.55 \quad (15)$$

$$C = \log(\text{Ca}(\text{mg CaCO}_3/\text{L})) - 0.4 \quad (16)$$

$$D = \log \text{Alk}(\text{mg CaCO}_3/\text{L}) \quad (17)$$

This simplified method for the calculation of pHsat continues to be used frequently as an indicator of the tendency of water to dissolve or precipitate calcium carbonate. However, it is an empirical method that does not include a series of calculations of the thermodynamics of the process that should be considered in a complete analysis of the factors intervening in reaction [10].

### 2.2. SM2330 method for the calculation of pHsat

The standard SM2330 method [10] summarises the progress made to date in water chemistry and is the internationally accepted method for the calculation of pHsat.

The SM2330 method is a more accurate and precise model that includes thermodynamic concepts of reaction [10].

The SM2330 method implies correcting the original Langelier formula with the coefficient for the activity:

$$\text{pHsat} = \text{p}K_2 + \text{p}K_{\text{sc}} + \text{pCa}^2 + \text{pAlk} + 5\text{pfm} \quad (18)$$

where  $K_2$  = second constant of disassociation for carbonic acid of water temperature;  $K_{\text{sc}}$  = product of solubility for calcite at water temperature;  $\text{Ca}^{2+}$  = calcium, in mols-g/L; Alk = alkalinity, in equivalents-g/L.

The following equations are proposed for calculation of each of the elements of the equation:

$$\text{p}K_2 = 107.8871 + 0.03252849T - 5,151.79 / T - 38.92561 \log 10T + 56,3713.9 / T2 \quad (19)$$

for a temperature range of 273–373 K.

$$\text{p}K_{\text{sc}} = 171.9065 + 0.077993T - 2,839.319 / T - 71.595 \log 10T \quad (20)$$

for a temperature range of 273–363 K.

$$\text{pfm} = A \left( \frac{I^{0.5}}{1 + I^{0.5}} \right) - 0.3I \quad (21)$$

valid for  $I < 0.5$ .

where:

$$I = 1.6 \times 10^{-5} \times \text{CE}_{25} \quad (22)$$

$$A = 1.82 \times 10^6 (E \times T) - 1.5 \quad (23)$$

$$E = \left[ \frac{60,954}{T + 116} \right] - 68.937 \quad (24)$$

where  $I$  = ionic strength;  $\text{EC}_{25}$  = electrical conductivity,  $\mu\text{mhos/cm}$  or  $\mu\text{S/cm}$ ;  $T$  = temperature of water,  $K (^{\circ}\text{C} + 273.3)$ ;  $E$  = dielectric constant.

LSI calculation method according to SM2330 [10].

## 3. Results and discussion

### 3.1. Balance with carbon dioxide in the atmosphere

The data in Figs. 1 and 2 show that remineralised water tends to balance with a CO<sub>2</sub> content of around 0.7 + –0.1 mg of CO<sub>2</sub> per litre, for a temperature range between 14°C and 25°C [1]. It should be noted that the concentration of CO<sub>2</sub> in the atmosphere is equivalent to approximately 0.56 mg of CO<sub>2</sub> per litre [1,3]. A total of 9 water samples were taken in 5 different desalination plants: Plant 1 (one sample), Plant 2A (three samples), Plant 2B (two samples), Plant 3A (two samples) and Plant 3B (one sample).

Fig. 1 shows a series of plants where the output  $\text{CO}_2$  is less than 0.7 mg of  $\text{CO}_2$  per litre, which suggests that not enough  $\text{CO}_2$  has been dosed and consumed during the remineralization process. Therefore, water tends to absorb  $\text{CO}_2$  from the atmosphere until it is balanced with it. In Fig. 2 the phenomenon is the opposite, with the output  $\text{CO}_2$  content higher than that of the atmosphere. Therefore, there is a loss of  $\text{CO}_2$  from the water until it reaches equilibrium. Comparing the data in Figs. 1 and 2, the equilibrium pH, which corresponds to the pH of the acid–base chemical equilibrium of Eq. (2) explained in section 2, of the desalinated water is around 0.3 mg of  $\text{CO}_2$  per litre instead of 0.7 mg of  $\text{CO}_2$  per litre as in remineralized water. The equilibrium pH is obtained from analysis of the acid–base chemistry and in accordance with the Henderson–Hasselbach formula [1,4].

### 3.2. Mathematical simulation of remineralization

To better analyse this phenomenon of interaction between desalinated and remineralized water in equilibrium with the atmosphere, two mathematical simulations of the remineralization process have been carried out [1,4,5]. Firstly, desalinated water was used (200 mg TDS/L; pH 6.2; 0.5 mg  $\text{Ca}^{2+}$ /L; 4.5 mg  $\text{CaCO}_3$ /L; 20°C) and the pH was increased with caustic soda to demonstrate that the lack of calcium is an unsurmountable factor that does not allow an LSI of zero to be achieved even if the pH is increased.

As can be seen in Fig. 3, at a  $\text{CO}_2$  concentration of 0.7 mg/L, where the water would be in equilibrium with the atmosphere, the pH of the water reaches a value of around 7 and the LSI remains negative at around  $-4$  to  $-3$ . The  $\text{pH}_{\text{sat}}$ , the  $\text{pH}_{\text{eq}}$  and the water pH cross at a pH of 12 [1,6,7].

The difference between  $\text{pH}_{\text{eq}}$  and  $\text{pH}_{\text{sat}}$  can be seen in Fig. 3. If the solution is saturated with calcite and it is at the acid–base equilibrium pH,  $\text{pH}_{\text{eq}}$  coincides with  $\text{pH}_{\text{sat}}$  and LSI is equal to zero.

Secondly, remineralized water was used with 300 mg TDS/L, 22 mg  $\text{Ca}^{2+}$ /L, 60 mg  $\text{CaCO}_3$ /L of alkalinity, a temperature of 20°C and at pH seven, and the pH was increased with caustic soda to also see the evolution of the saturation pH balance and the LSI.

In Fig. 4 it can be seen, in this case, that the saturation pH, the equilibrium pH and the pH of the water cross at a value close to 8.2 where the LSI is zero, and it can also be seen that at this pH the  $\text{CO}_2$  content is around 0.7 mg of  $\text{CO}_2$  per litre. This would be the condition where, in theory, this water will remain stable with the atmosphere, also conserving the LSI equal or very close to zero.

In the following simulation, different quantities of  $\text{CO}_2$  were dosed into a desalinated water and left in equilibrium with calcite until the saturation pH and therefore an LSI of zero were reached. Fig. 5 shows the evolution of pH, calcium, and  $\text{CO}_2$  in water with different degrees of remineralization and in equilibrium with calcite [1,4–7].

In a situation of equilibrium (LSI equal to zero), the value of 0.7 mg of  $\text{CO}_2$ /L corresponds to an alkalinity of 64 mg of  $\text{CaCO}_3$ /L per litre and a pH of 8.24 and 24.7 mg of  $\text{Ca}^{2+}$ /L. These values are, as expected, in line with those of Fig. 4.

The variation in the composition of the desalinated water from various desalination plants is illustrated in the results of Table 2.

### 3.3. Obtaining the pH in equilibrium with the $\text{CO}_2$

Fig. 6 illustrates the relationship between water pH and  $\text{CO}_2$  content for remineralized water, based on the data collected.

Based on the regression in Fig. 6 obtained from the laboratory data and Eq. (7), it can be calculated that for a  $\text{CO}_2$  content of 0.7 mg/L the pH of the remineralized water would be around 8.09.

Table 1  
Equations and methods for the remineralization of desalinated waters

	Remineralisation process	Process reaction	Consumption of chemical products per 1 unit increase in alkalinity	Increase in anion and cation content per mol/m <sup>3</sup> of alkalinity
1	Calcium carbonate + Carbon dioxide	$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + 2(\text{HCO}_3^-)$	50.1 mg $\text{CaCO}_3$ 100% 22 mg $\text{CO}_2$	20 mg $\text{Ca}^{2+}$
2	Calcium hydroxide + Carbon dioxide	$\text{Ca}(\text{OH})_2 + 2\text{CO}_2 \leftrightarrow \text{Ca}^{2+} + 2(\text{HCO}_3^-)$	37.1 mg $\text{Ca}(\text{OH})_2$ 100% 44 mg $\text{CO}_2$ /L	20 mg $\text{Ca}^{2+}$
3	Dolomite + Carbon dioxide	$\text{MgO} \cdot \text{CaCO}_3 + 3\text{CO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{Mg}^{2+} + \text{Ca}^{2+} + 4(\text{HCO}_3^-)$	35.1 mg $\text{MgO} \cdot \text{CaCO}_3$ 100% 33 mg $\text{CO}_2$	6.1 mg $\text{Mg}^{2+}$ 10 mg $\text{Ca}^{2+}$
4	Calcium carbonate + Sulphuric acid	$2\text{CaCO}_3 + \text{H}_2\text{SO}_4 \leftrightarrow \text{Ca}^{2+} + 2(\text{HCO}_3^-) + \text{Ca}(\text{SO}_4)$	100.1 mg $\text{CaCO}_3$ 100% 49 mg $\text{H}_2\text{SO}_4$ 100%	40.1 mg $\text{Ca}^{2+}$ 48 mg $\text{SO}_4^{2-}$
5	Calcium chloride + Sodium bicarbonate	$\text{CaCl}_2 + 2\text{NaHCO}_3 \leftrightarrow \text{Ca}^{2+} + 2(\text{HCO}_3^-) + 2\text{NaCl}$	55.5 mg $\text{CaCl}_2$ (100%) 84 mg $\text{NaHCO}_3$ (100%)	23 mg $\text{Na}^+$ 20 mg $\text{Ca}^{2+}$ 35.5 mg $\text{Cl}^-$

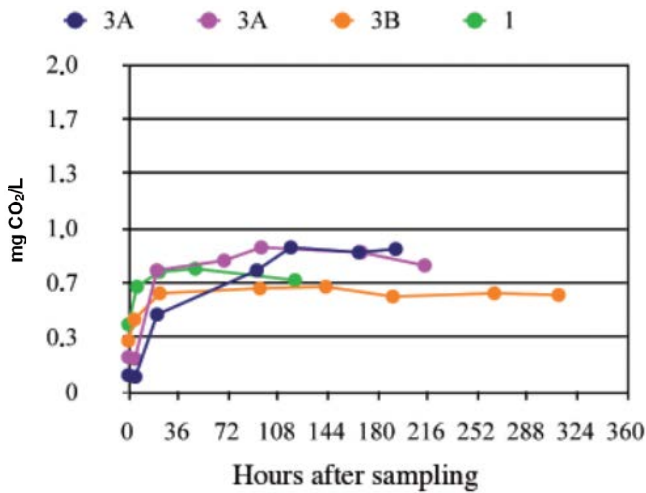


Fig. 1. Evolution of CO<sub>2</sub> of remineralised water from various desalination plants with infra-dosing of CO<sub>2</sub>.

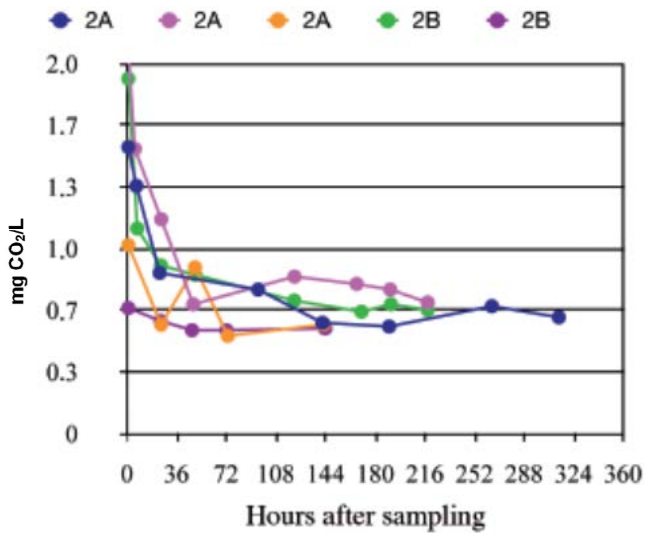


Fig. 2. Evolution of CO<sub>2</sub> of remineralised water from various desalination plants with slight overdosing of CO<sub>2</sub>.

This is a value very close to the 8.24 obtained with the theoretical simulation procedure described in the previous subsection [1–3].

Fig. 15, at the end of section 3, also presents the results obtained and shows the clear relationship between both parameters. This relationship corresponds practically to the formula presented by Tillmans and published in 1912 [1,3], where the concentrations of CO<sub>2</sub> and alkalinity are expressed in mg/L.

### 3.4. Evolution of the pH and LSI of the remineralized water

In accordance with the field data, Figs. 7–12 show the evolution of the pH and LSI for remineralized water from the different desalination plants grouped using the same criteria as Figs. 1 and 2.

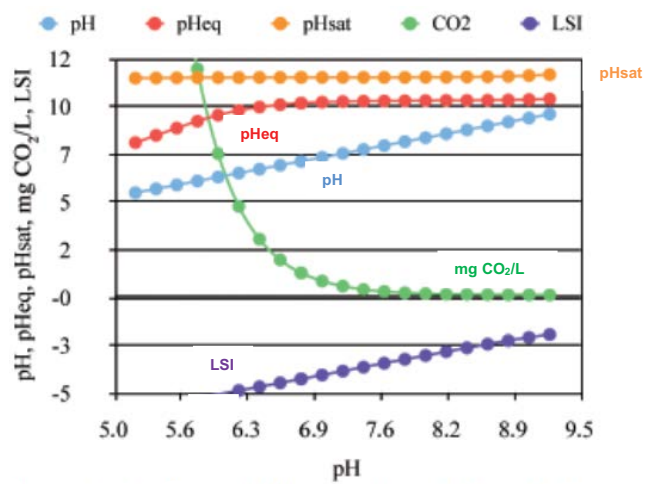


Fig. 3. Evolution of different values of pH and LSI of desalinated water with the addition of Na(OH).

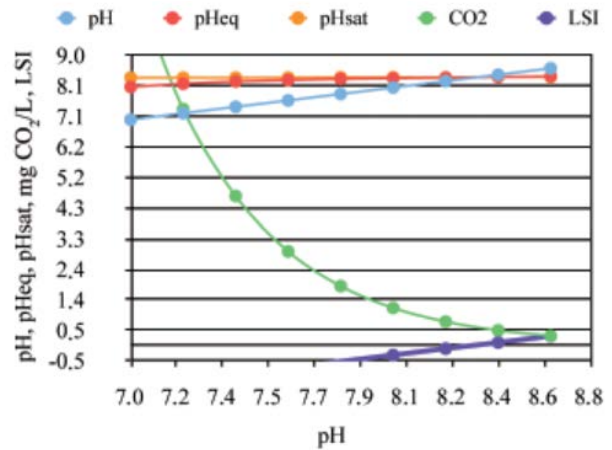


Fig. 4. Evolution of different values of pH and LSI with the addition of Na(OH) to a water with 20 mg Ca<sup>2+</sup>, 60 mg CaCO<sub>3</sub>, 20°C and starting at pH of 7.

The data in Fig. 7 shows that the pH drops to equilibrium as the water balances with the CO<sub>2</sub> in the atmosphere.

The decrease in pH is more accentuated the lower the remineralization, for example lower CO<sub>2</sub> dosage (Plant 3A).

Figs. 9 and 10 complement the data in Fig. 7 for bicarbonates and LSI respectively.

The data in Fig. 8, on the other hand, show that the pH rises when remineralization is excessive, as the water loses CO<sub>2</sub>.

The greater the overdose of CO<sub>2</sub>, the greater the rise in pH after remineralization. Figs. 11 and 12 complement the data in Fig. 8 for bicarbonates and LSI respectively. The data in Fig. 11 also confirms that the equilibrium values of the remineralized water are around 73 ± 4 mg bicarbonate per litre (L) and the pH around 8.2. These data coincide with the data obtained by the simulation [1,4–7].

### 3.5. Relationship between alkalinity and CO<sub>2</sub> dosage

Fig. 13 illustrates the relationship between the alkalinity of a remineralized water and the required dosage of

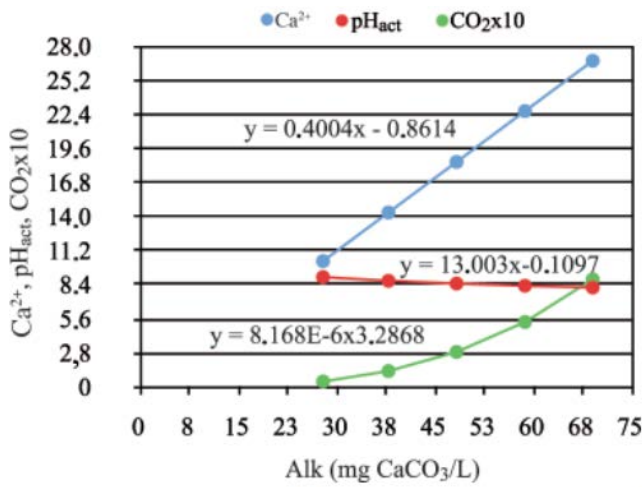


Fig. 5. Simulation of the composition of waters with different degrees of remineralisation and with LSI = 0.

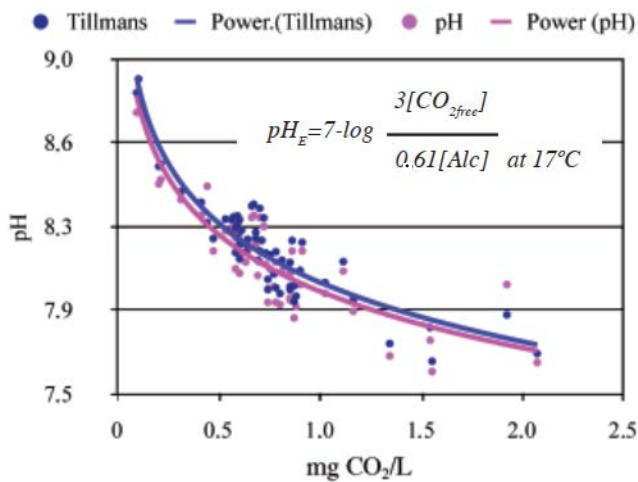


Fig. 6. Relationship between pH and CO<sub>2</sub> for remineralised waters in accordance with laboratory data and calculation using the Tillmans formula.

CO<sub>2</sub>, assuming that there is no loss of CO<sub>2</sub> after the exit of the reverse osmosis frame and that the efficiency is 100 × 100. These data were obtained by mathematical simulation and for a water with total dissolved solids of 180 mg/L, 1.5 mg/L of calcium and 20°C [1,4–7].

Establishing a target pH of 8.2 and a CO<sub>2</sub> content after remineralization of 0.7 mg CO<sub>2</sub>/L, under normal conditions the alkalinity of the permeate is usually around 1–2 mg of calcium carbonate per litre and so, depending on the pH of the permeate, the dose of CO<sub>2</sub> can be between 12 and 24 mg CO<sub>2</sub>/L.

### 3.6. Effect of temperature on remineralization

Fig. 14 illustrates the relationship between the alkalinity of a water with different levels of remineralization and the LSI, at different temperatures and for an open system, that is, in equilibrium with the atmosphere.

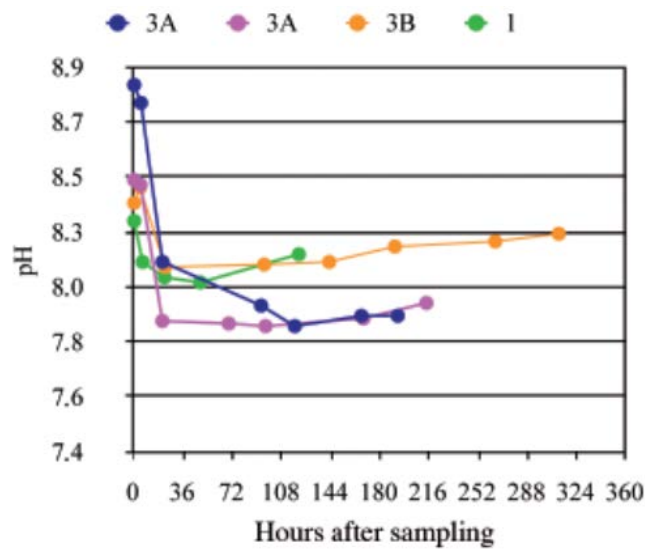


Fig. 7. Evolution of pH in remineralised water from various desalination plants with infra-dosing of CO<sub>2</sub>.

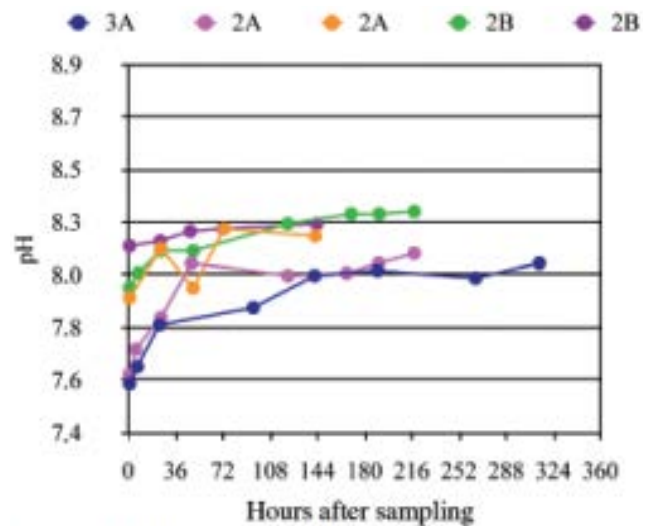


Fig. 8. Evolution of pH in remineralised water from various desalination plants with slight overdosing of CO<sub>2</sub>.

The data were obtained by mathematical simulation and refer to a remineralization with CO<sub>2</sub> and calcite bed [1,5–7].

The hardness and alkalinity of desalinated water are obtained through reaction (3).

However, with an increase in the CO<sub>2</sub> content of the water the slope of the curve is gradually flattened, thus allowing for more accurate dosing. It should be remembered that the accuracy achieved with this system is around ±2 mg CaCO<sub>3</sub>/L. In any case, the process is difficult to control.

A direct relation between the increase of alkalinity and the increase of the LSI is observed in Fig. 14.

The alkalinity obtained by adding more CO<sub>2</sub> implies an excess of CO<sub>2</sub> after remineralization. This excess CO<sub>2</sub> is lost at the exit of the plant as the water balances with the atmosphere. Thus, the LSI becomes positive.

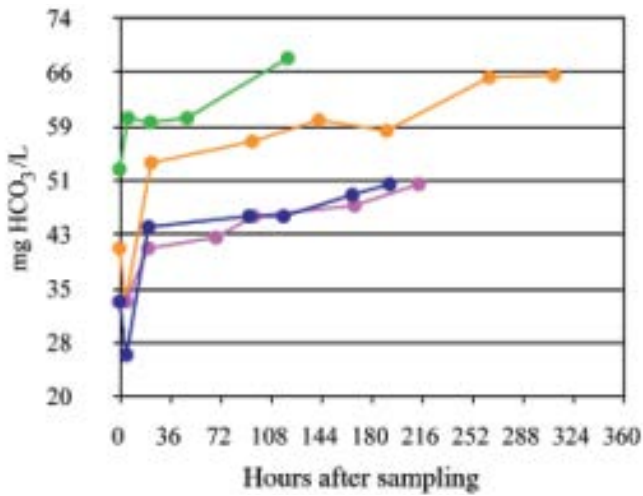


Fig. 9. Evolution of HCO<sub>3</sub><sup>-</sup> in remineralised water from various desalination plants with infra-dosing of CO<sub>2</sub>.

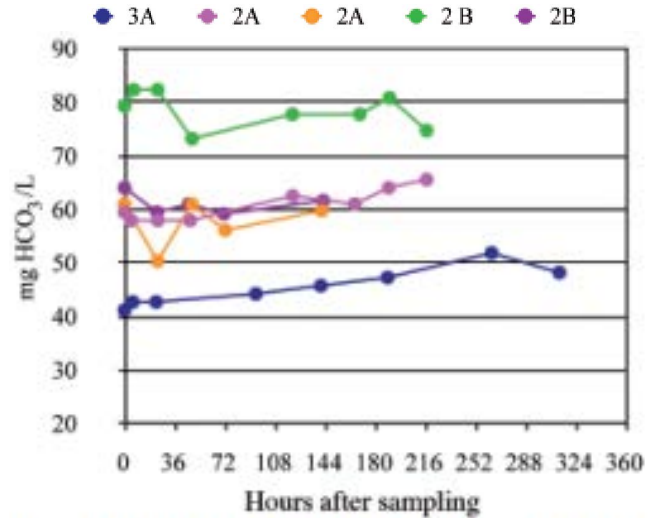


Fig. 11. Evolution of HCO<sub>3</sub><sup>-</sup> in remineralised water from various desalination plants with slight overdosing of CO<sub>2</sub>.

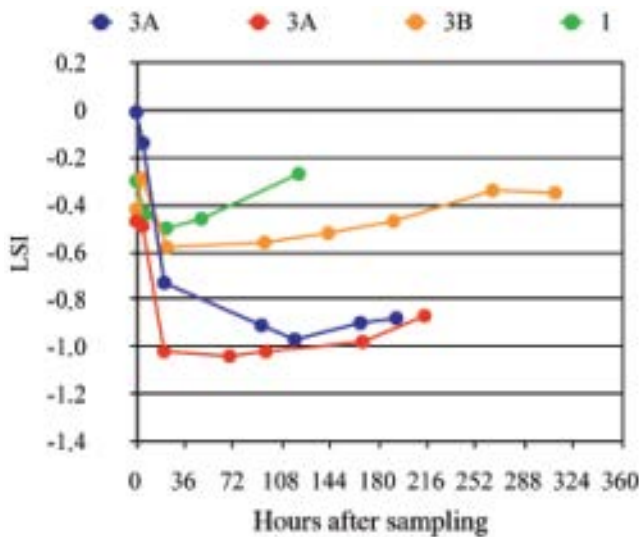


Fig. 10. Evolution of LSI in remineralised water from various desalination plants with infra-dosing of CO<sub>2</sub>.

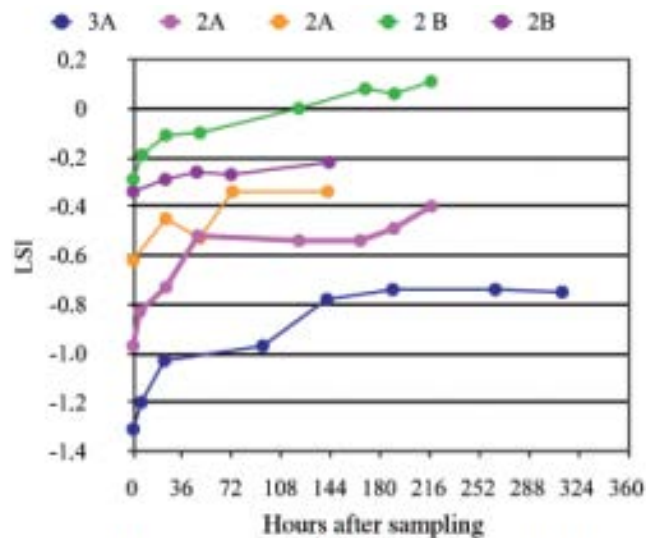


Fig. 12. Evolution of LSI in remineralised water from various desalination plants with slight overdosing of CO<sub>2</sub>.

In turn, a temperature increase further augments this effect, as the dissolved CO<sub>2</sub> decreases with increasing temperature. The effect of temperature changes on the LSI in the working ranges in desalination plants is in the order of  $\pm 0.1$  LSI. It can also be observed in Fig. 14 that a water re-mineralized to 100 mg of calcium carbonate per litre of alkalinity and at 40°C does not exceed the LSI value equal to 0.7 once it is balanced with the atmosphere. 40 mg/L of calcium corresponds to this level of remineralization [13–15].

At this point it should be clarified that, as has been indicated by other authors, remineralized waters do not precipitate easily even if the LSI reaches values of 0.7 and the temperature 40°C provided that the pH does not exceed 8.4 after remineralization [1,2]. This is relatively easy to achieve with calcite beds, though it is not so easy with calcium hydroxide treatments.

#### 4. Conclusions

According to this study, it is considered that remineralised water should have the conditions presented in Table 3 for a temperature range between 14°C and 25°C.

There is an option to add more CO<sub>2</sub> to increase alkalinity and hardness, but then the remaining CO<sub>2</sub> will be excessive to be in balance with the atmosphere and will be lost in a few hours causing the pH to rise and thus obtain a positive LSI. The effect of temperature changes on the LSI in the operating ranges of desalination plants is in the order of  $\pm 0.1$  LSI. In many water distributions networks, LSI values of between +0.1 and +0.5 are required to protect the facilities. This is achieved by slightly increasing the pH after calcite post-treatment with the addition of caustic soda (2–4 mg/L of caustic soda).

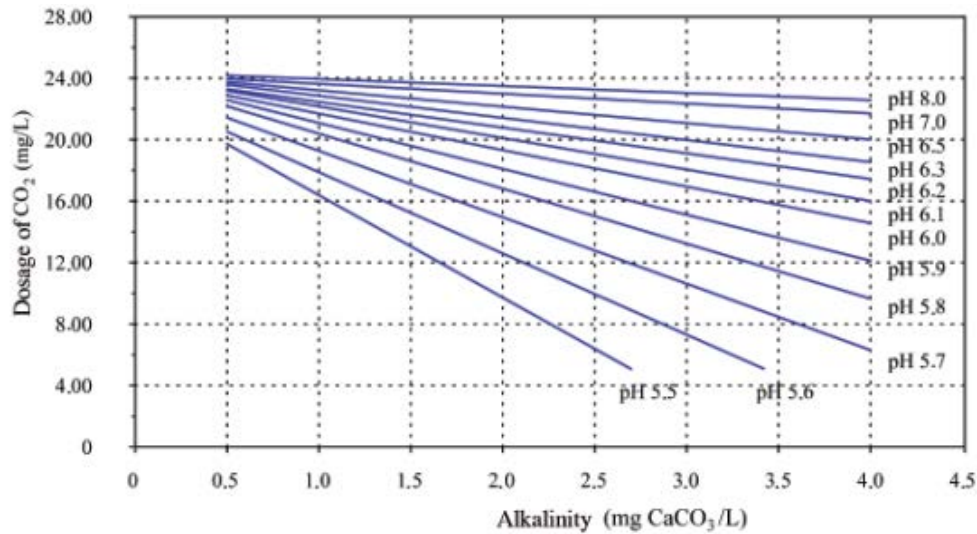


Fig. 13. Relationship between alkalinity and the dosage of  $\text{CO}_2$  to achieve a remineralised water at pH 8.2 and  $0.7 \text{ mg CO}_2/\text{L}$  with a calcite contactor. Simulated data from desalinated water with  $180 \text{ mg TDS/L}$ ,  $1.5 \text{ mg Ca}^{2+}/\text{L}$  and  $20^\circ\text{C}$ .

Table 2

Average composition of desalinated waters from 6 desalination plants under normal operating conditions

	Plant 1	Plant 2A	Plant 2B	Plant 3A	Plant 3B	Plant 4	Average	STD	Sea water <sup>10,11,12</sup>
Date	02/07/09	04/06/09	Average 04/06/09 y 26/06/09	Average 2/06/09 y 12/6/09	11/06/09	October and November 2008 average	Average	Standard deviation	Average-values of the Western Mediterranean
pH	6.60	5.52	5.22	5.35	5.29	5.92	5.65	0.48	7.9–8.3
$\text{CE}_{257}$ $\mu\text{S/cm}$	667	584	240	693	358	670	535.28	209.14	56,000
$\text{HCO}_3^-$ , mg/L	1.96	1.48	0.82	1.97	1.1	2.4	1.62	0.54	140
$T^{\text{h}}$ , $^\circ\text{C}$	23.5	22.1	22.1	23.5	22.6	22.0	22.63	0.80	14–28
$\text{CO}_2$ , mg/L	0.75	7.82	11.63	15.94	9.89	4.65	8.46	4.87	90
$\text{Ca}^{2+}$ , mg/L	1.20	1.54	1.90	1.18	0.95	1.80	1.43	0.34	400
$\text{Mg}^{2+}$ , mg/L	2.30	2.00	2.68	2.66	1.77	2.90	2.39	0.32	1,300
$\text{Na}^+$ , mg/L		90.12	35.60	107.20	58.25		72.79	32.04	10,550
$\text{K}^+$ , mg/L		3.85	1.46	5.30	3.62		3.56	1.59	380
$\text{Cl}^-$ , mg/L		168.11	63.96	203.50	107.70		135.82	62.12	18,980
$\text{NO}_3^-$ , mg/L		0	0	0	0		0	0	<0.7
$\text{SO}_4^{2-}$ , mg/L		4.28	4.65	5.34	8.80		5.77	2.07	2,650
$\text{RS}_{180}$ , mg/L		274	97	340	172		220.65	107.56	
$\text{RS}_{180}/\text{CE}_{25}$		0.47	0.41	0.49	0.48		0.46	0.04	
$\text{STD}_{\text{a+c}}$ , mg/L		274.48	117.6	325.71	168.26		221.51	95.39	
$\text{STD}_{\text{a+c}}/\text{CE}_{25}$		0.47	0.49	0.47	0.47		0.47	0.01	
Turbidity, NTU	0.20	0.30	0.21	0.18	0.18		0.21	0.05	
Langelier (SM2330)	-4.49	-5.55	-5.83	-5.70	-5.90	-5.26	-5.46	0.48	
Larson-Skold		164	115	149	179		152	27	
SAR		11.28	3.90	12.51	8.15		8.96	3.33	
pHeq with $\text{CaCO}_3$	9.79	9.08	8.76	8.62	8.90	9.35	9.08	0.40	

pH, CE,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and temperature analyzed *in situ*. Other parameters analyzed in the laboratory are average values for each desalination plant.



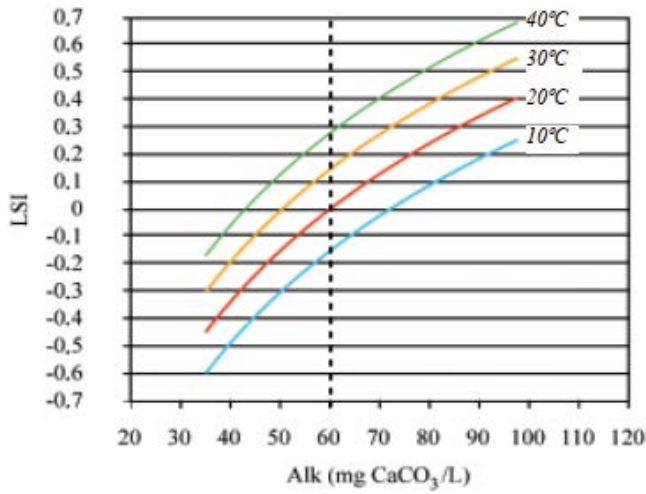


Fig. 14. Relationship between LSI and alkalinity for remineralised waters from different temperatures simulated data.

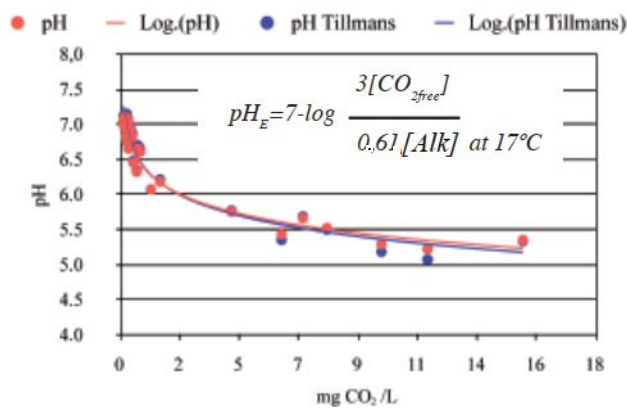


Fig. 15. Relationship between CO<sub>2</sub> content and pH in desalinated waters according to data analysed in the laboratory and those calculated with the Tillmans formula.

Table 3  
Characteristics recommended for desalinated waters with an optimum level of remineralisation

Parameter	Range
pH	8.2 ± 0.1
Alk (mg CaCO <sub>3</sub> /L)	56 ± 3
Ca <sup>2+</sup> (mg/L)	21 ± 2
CO <sub>2</sub> (mg/L)	0.7 ± 0.1
LSI	±0.15

In installations with calcium hydroxide, this is achieved by slightly overdosing with calcium hydroxide. On some occasions, technical limitations in the control of the exact dosage of calcium hydroxide can generate an increase of the turbidity above 1 NTU. This excess turbidity could result in the precipitation of calcium in the pipes and a consequent reduction of their internal diameter. Moreover, in the case of a second pass of reverse osmosis with this water the membrane supplier strongly requires a turbidity lower than 1 NTU.

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