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Characteristics of desalinated water in reverse osmosis plants in Spain

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ABSTRACT

In this study on desalinated water characteristics, the mean total dissolved salts content is 280 mg/L, of which approximately 72% is NaCl. The HCO_3^- (<4 mg HCO_3^-/L), Ca^{2+} (2.5 mg Ca^{2+}/L) and Mg^{2+} (<4 mg Mg^{2+}/L) contents are all low. The Mg^{2+} content is approximately twice that of Ca^{2+}, both expressed in mg/L. The pH at the outlet of the reverse osmosis racks ranges from 5.2 to 6.7, depending on the plant. CO_2 content varies between 0.8 and 16 mg CO_2/L. Certain waters may move outside this range because of specific treatments. Permeates with high pH are related to the need to increase boron rejection. The data obtained corroborate the logarithmic ratio established in the literature between the pH of desalinated water and its CO_2 content. Desalinated water has a Langelier Saturation Index (LSI) of less than –4, because of which it tends to dissolve calcium carbonate. This also implies the risk of problems of corrosion due to its higher chlorine (60–200 mg Cl/L) and sulfate content (2–5.7 mg SO_4^{2-}/L) compared to its content of bicarbonates (2–4 mg HCO_3^-/L). The pH of desalinated water quickly balances with the CO_2 content of the atmosphere, so that it should be analyzed carefully and preferably *in situ*. In equilibrium with the atmosphere, the pH of desalinated water is between 6.9 and 7.0 and its CO_2 content around 0.3 mg CO_2/L. The LSI remains at around –4. The turbidity of desalinated water is around 0.2 NTU, and higher values may be an indication of problems in the facilities. The sodium adsorption ratio of desalinated water is equal to or higher than 9, indicating that it may be harmful to the structure of agricultural soils and cause problems of toxicity for certain crops due to the excess of Na^+ with respect to Ca^{2+} and Mg^{2+}. Finally, the results suggest that desalinated water generally does not contain sufficient CO_2 to permit adequate remineralization without extra input of CO_2.

Keywords: Remineralisation; Reverse osmosis; Desalination; Water characteristics

1. Introduction

The composition of desalinated water varies according to the type of plant and the way it is operated. The addition of acids or bases prior to the desalinated system varies the pH of the permeate and, therefore, its CO_2 content [1,2]. The state of the membranes also affects the degree of salt rejection of the different components. Consequently, the amount of total dissolved solids (TDS) and the electrical conductivity (EC) also vary.

In this paper, a study is undertaken of desalinated water characteristics, which are very important depending on the freshwater demand and the quality needed. Due to this, it is necessary to know very well the characteristics of the desalinated water for its remineralization and to meet the required water quality [1,3–5].

Desalinated waters are a solution with a high proportion of ClNa. The data obtained in this article corroborate the logarithmic ratio established in the literature between the pH of desalinated water and its CO_2 content. Desalinated water

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generally does not contain sufficient CO_2 to permit adequate remineralization without extra input of CO_2 [1,6–8].

The overall objective of this article is to illustrate, based primarily on field data, the criteria used to properly assess the quality of desalinated and remineralized water, thus facilitating compliance with EU regulations for water supply (Spanish RD 140/2003) [1,6].

In particular, the specific objective of the article is to establish the criteria for the sampling and calculation of analytical results to correctly define the quality of desalinated and remineralized water.

2. Material and methods

For the study of the desalinated water, samples were taken in different desalination plants and *in situ* analyses were carried out of pH, electrical conductivity, temperature, HCO_3^- and CO_3^{2-}.

The samples were then taken to the laboratory where the analyses were repeated and completed along with the rest of the parameters [1]. Samples were taken for analysis every few days, up to 14 times.

In this article, the water analysed comes directly from the desalination process [9]. Therefore, "desalinated water" always refers to "non-remineralized water". Desalinated water is also called permeate.

This work was undertaken after an extensive bibliographical survey, with special attention paid to quality standards and analytical methods [8,9]. A series of analyses were carried out on desalinated and remineralized waters from different desalination plants to study their behaviour in contact with the atmosphere [6,7,10].

The following parameters are considered in the article [2].

- LSI: Langelier Saturation Index
- SAR: sodium adsorption ratio
- EC: electrical conductivity
- pHsat: saturation pH
- pHeq: equivalent pH

In particular, calculation of the LSI and the saturation pH (pHsat) were undertaken following the most common evaluation criteria [1,2].

Specific data are also used to examine the characteristics of remineralized waters and their behaviour in contact with the atmosphere, the ultimate aim being to define optimum levels of remineralization guaranteeing a stable LSI and a minimum consumption of CO_2 [1].

To ensure optimum evaluation of the results, specific mathematical simulations were performed on water remineralization and mixes, using scientifically sound calculation programmes [11].

An important part of the work is oriented towards investigating changes in the composition of remineralized waters with respect to desalinated waters, with a view to developing a procedure for indirect calculation of the LSI and other indices based on the increases in EC and pH caused by remineralization [12–15].

A total of 8 seawater desalination plants were visited to take samples of desalinated water, 6 of which (1A, 2A, 2B, 3A, 3B, and 4) operate without increasing pH and 2 of which (5 and 6) increase pH to improve boron rejection in the permeate [16,17].

3. Results and discussion

The variation in the composition of the desalinated water from the various desalination plants is illustrated in the results of Table 1.

These results were extracted from the data analysed and reflect a range of values frequently found in reverse osmosis (RO) desalination plants. The characteristics of all 8 plants considered in this study are presented in Table 2.

Table 1 includes the average values of the pH, EC, HCO_3^-, CO_3^{2-} and temperature analyzed *in situ*. As these are samples *in situ* and carefully analysed to avoid loss of CO_2, it can be assumed that they reflect the quality conditions of the permeate at the outlet of the frame.

Table 3 shows the data of two other desalination plants where the pH of the raw water before the rack was raised to increase boron rejection by the RO membranes.

Comparing Tables 1 and 3, it is possible to explain in detail the results presented in both tables. Tables 1 shows the average composition of desalinated waters from six desalination plants under normal operating conditions, with pH, CE, HCO_3^-, CO_3^{2-} and temperature analyzed *in situ*. The other parameters were analyzed in the laboratory, with the average values for each desalination plant shown. Table 3 shows the average composition of desalinated waters from 2 desalination plants in which the pH had been increased to increase boron rejection by the RO membranes.

Table 1 shows the results from 6 seawater desalination plants (1A, 2A, 2B, 3A, 3B, and 4), all operating in 1 or 2 steps without a second pass and without increasing the pH to increase boron rejection of the permeate water produced. Table 3 shows the results from the other 2 seawater desalination plants (5 and 6) considered in the study, in which the pH is raised to increase boron rejection.

The average content of Na in the permeate of the seawater desalination plants included in Table 1 is 72.9 mg/L. However, the content of Na in the permeate of seawater desalination plant number 6 included in Table 3 is 23.6% higher (95.4 mg/L) due to the increase of the pH with caustic soda to improve boron rejection.

These waters have a pH higher than 8 and sometimes up to 10 (plant 5). However, they retain all the other typical characteristics of desalinated water, most notably a TDS content of less than 300 mg/L with 72% sodium chloride.

In Table 1, a certain variation in EC can be observed. This variation is related to specific situations within the process, such as the case of plant 2B where the performance of the membranes is abnormally high or, as occurs in plant 5 in Table 3, due to the existence of a second pass.

The normal EC value in a single-pass RO system is between 500 and 700 μS/cm. In double-pass plants, part of the permeate is desalinated again and then mixed at the outlet. In these cases, the EC varies between 80 and 400 μS/cm.

In any case, the quality of the desalinated water depends on several factors such as the physicochemical pre-treatment, the temperature of the water and the chemical composition of the raw water. Therefore, each case would require a detailed study that is beyond the scope of this article.

Table 1
Average composition of desalinated waters from six desalination plants under normal operating conditions

	Plants						Average	STD	Seawater
	1	2A	2B	3A	3B	4			
Parameters									
pH	6.60	5.52	5.22	5.35	5.29	5.92	5.65	0.48	7.9–8.3
EC_{25}, μS/cm	667	584	240	693	358	670	535.28	209.14	56,000
HCO_3^-, mg/L	1.96	1.48	0.82	1.97	1.1	2.4	1.62	0.54	140
T, °C	23.5	22.1	22.1	23.5	22.6	22.0	22.63	0.80	14–28
CO_2, mg/L	0.75	7.82	11.63	15.94	9.89	4.65	8.46	4.87	90
Ca^{2+}, mg/L	1.20	1.54	1.90	1.18	0.95	1.80	1.43	0.34	400
Mg^{2+}, mg/L	2.30	2.00	2.68	2.66	1.77	2.90	2.39	0.32	1,300
Na^+, mg/L		90.12	35.60	107.20	58.25		72.79	32.04	10,550
K^+, mg/L		3.85	1.46	5.30	3.62		3.56	1.59	380
Cl^-, mg/L		168.11	63.96	203.50	107.70		135.82	62.12	18,980
NO_3^-, mg/L		0	0	0	0		0	0	<0.7
SO_4^{2-}, mg/L		4.28	4.65	5.34	8.80		5.77	2.07	2,650
RS_{150}, mg/L		274	97	340	172		220.65	107.56	
RS_{150}/EC_{25}		0.47	0.41	0.49	0.48		0.46	0.04	
STD_{a+c}, mg/L		274.48	117.6	325.71	168.26		221.51	95.39	
STD_{a+c}/EC_{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 $CaCO_3$	9.79	9.08	8.76	8.62	8.90	9.35	9.08	0.40	

pH, EC, HCO_3^-, CO_3^{2-} and temperature analyzed *in situ*. The other parameters were analyzed in the laboratory. The average values for each desalination plant are shown.

Detailed information on seawater quality, desalination systems and their relation to desalinated water quality can be found in specific literature [2–7].

3.1. On the CO_2-pH ratio in desalinated water

Table 1 shows a pH variation in the plants of between 5.22 and 6.6 and a CO_2 content variation of between 0.75 and 16 mg CO_2/L.

These data reflect the relationship between CO_2 and pH.

Fig. 1 presents the results obtained and shows the clear relationship between the two parameters. This ratio practically corresponds to the Tillmans formula [11], where the concentrations of CO_2 and alkalinity are expressed in mg/L.

Calcium carbonate solubility equilibrium is highly important in many phases of water chemistry. It is directly associated with scale formation in many types of equipment, from tea kettles to boiler feed water heaters, and with incrustation of well screens, sand filters, meters and water taps. In physiological chemistry, it is significant in relation to bone calcification and to blood equilibriums. In geochemistry, the deposition of carbonates is also related to this equilibrium. The equilibrium balance is affected by many natural reactions in water, before, during and after the treatment process [11].

3.2. On the relationship between EC and the presence of Cl^- and Na^+

Desalinated water is a solution with around 72% Cl Na content. Thus, the conductivity of desalinated water is directly proportional to the increase in chloride and sodium. Fig. 2 shows this relationship.

Fig. 3 illustrates the ratio between chloride and sodium, which is 1.25 mMol Cl^- per mMol Na^+. Graphically it is shown how the chloride value increases with the sodium value, according to the data presented in Table 1. Therefore, Cl^- content is approximately 25% higher than Na^+ content, following the linear equation shown in Fig. 3.

This equation in Fig. 3 follows the linear formula, $y = ax + b$, where "a" and "b" are two constants, with:

- $a = +1.2574$
- $b = –0.1502$

3.3. On the contents of Ca^{2+} and Mg^{2+}

As shown in Fig. 4, the calcium and magnesium contents maintain a certain proportionality.

According to these data, and in an approximate way, it can be assumed that Mg^{2+} (mg/L) = 1.7 × Ca^{2+} (mg/L).

Table 2
General characteristics of the desalination plants included in Table 1

Parameters	Plant 1	Plant 2A	Plant 2B	Plant 3A	Plant 3B	Plant 4	Plant 5	Plant 6
Average age of membranes (years approx.)	7	6	2	1.5	2.5	5	Initially expected data	1.5
Type of post-treatment	Lime + CO_2 (without saturator) In-pipe dosing	Lime + CO_2 (without saturator) In-tank dosing	Lime + CO_2	Lime + CO_2 (with saturator) In-tank dosing	Lime + CO_2 (with saturator) In-tank dosing	Lime + CO_2 (with saturator) In-tank dosing		Lime + CO_2 (with saturator) In-tank dosing
Origin of raw water	Open intake. Mediterranean	Coastal wells mixed with fossil saline. Mediterranean	Coastal wells mixed with fossil saline. Mediterranean	Open intake. Mediterranean	Open intake. Mediterranean	Coastal wells. Atlantic	Coastal wells. Atlantic	Open intake. Mediterranean
Operation during sampling	Single step	Single step	Single step	Single step	Two steps	Single step	Two steps	Two steps

Table 3
Average composition of desalinated waters from 2 desalination plants in which the pH had been raised to increase boron rejection by the RO membranes

	Plant 5	Plant 6
Date	02-07-09	04-06-09
pH	10.0	8.6
EC_{25}, μS/cm	50	624
HCO_3^-, mg/L	0.1	1.2
CO_3^{2-}, mg/L	0.01	0.01
T, °C	22.0	20.3
CO_2, mg/L	0.00	0.00
Ca^{2+}, mg/L	0.20	0.94
Mg^{2+}, mg/L	2.3	1.80
Na^+, mg/L		95.39
K^+, mg/L		4.49
Cl^-, mg/L		168.71
NO_3^-, mg/L		0
SO_4^{2-}, mg/L		4.6
Turbidity, NTU		0.19
LSI (SM2330)	–3.05	-2.94
Larson–Skold		231
SAR		13.28

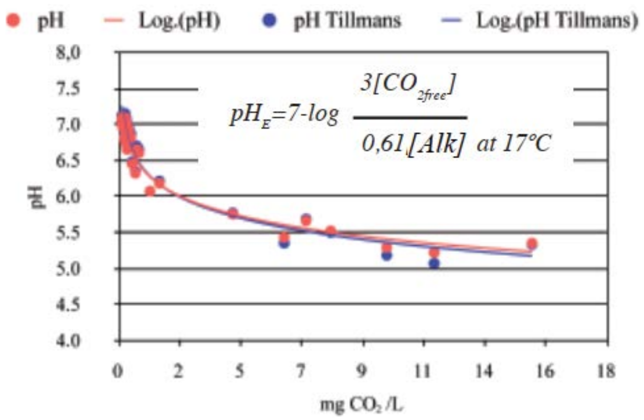

Fig. 1. Relationship between CO_2 content and pH in desalinated waters according to data analysed in the laboratory and those calculated with the Tillmans formula.

However, with the available data, a clear relationship between EC and calcium-magnesium content was not found.

3.4. Behaviour of desalinated water in contact with the atmosphere

The sensitivity of desalinated water to the quality of the sampling procedure is shown by the results of Figs. 5–7. According to these results, desalinated water tends to balance with the CO_2 in the atmosphere within a few hours. This requires extreme caution when interpreting the permeate samples, as the pH can be significantly affected in around 2 h.

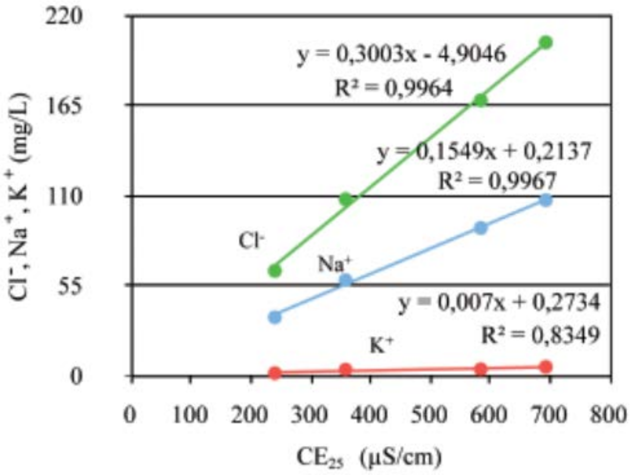

Fig. 2. Relationship between EC and Cl^-, Na^+ and K^+ contents. Data from Table 1.

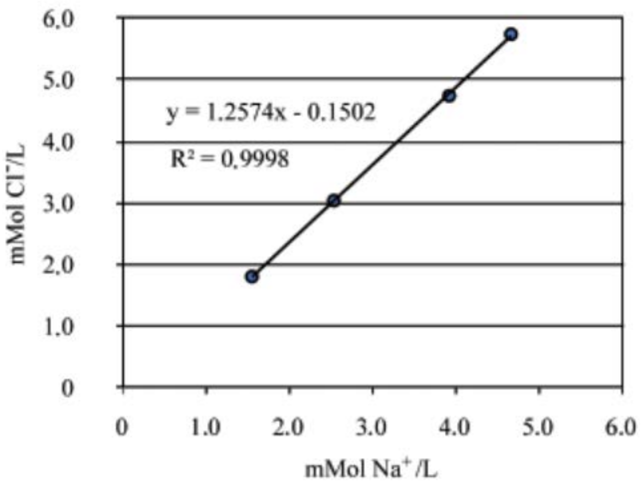

Fig. 3. Relationship between mMol of Cl^- and mMol of Na^+ according to data from Table 1.

Fig. 6 shows that desalinated water in equilibrium with the atmosphere contains about 0.3 mg of CO_2 per litre. This value contrasts with the value of 0.6–0.7 mg of CO_2 per litre for remineralised water. As can be deduced from Figs. 5 and 6, the drop in CO_2 content is very rapid and is related to the low alkalinity of desalinated water.

Fig. 8 illustrates the evolution of the LSI-2330 over time for the same data as in Fig. 5 [1,9].

As can be seen, the LSI-2330 remains at around –4, even after several days of the water being exposed to the atmosphere. The negative value of the LSI-2330 points to the fact that desalinated water maintains the tendency to dissolve calcium carbonate in an open system. Fig. 9, on the other hand, illustrates the relationship between the pH and the LSI-2330 using the data from Figs. 7 and 8. There is a clear relationship between the two parameters. The samples were kept exposed to the atmosphere and gently shaken in the laboratory following sampling [9].

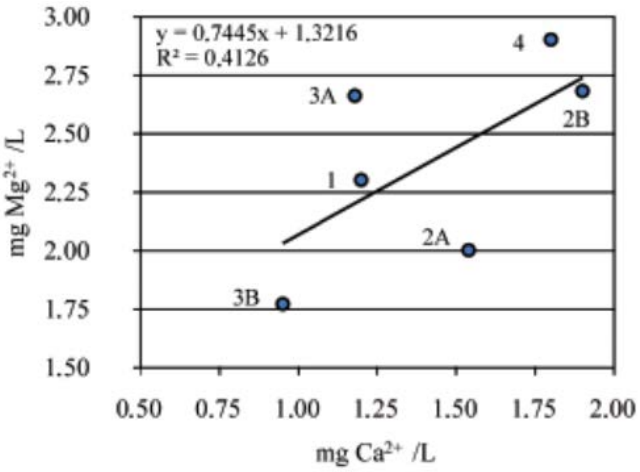

Fig. 4. Relationship between Ca^{2+} and Mg^{2+} according to data from Table 1.

3.5. On total dissolved solids

Table 1 shows the TDS values obtained by the traditional method of drying at 180°C and by the sum of anions and cations.

As can be seen, the difference between the average values obtained by the two methods is only 1 mg/L and therefore less than 1%.

It is noted, however, that the method of summation of anions and cations is more accurate since the method by drying at 180°C can produce small errors. In any case, the TDS value affects the LSI-2330 calculation very little, and selecting a value between 0.47 and 0.46 does not produce a significant difference [9].

3.6. On the turbidity of the desalinated water

The turbidity of water desalinated by reverse osmosis is low and around 0.2 NTU. Higher values of turbidity are

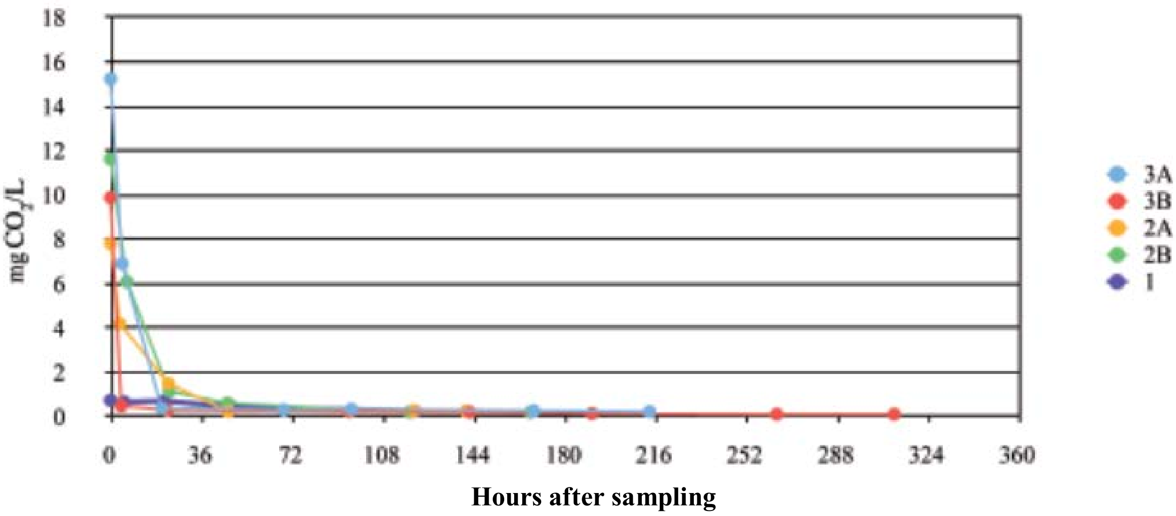

Fig. 5. Evolution of CO_2 content following permeate sampling.

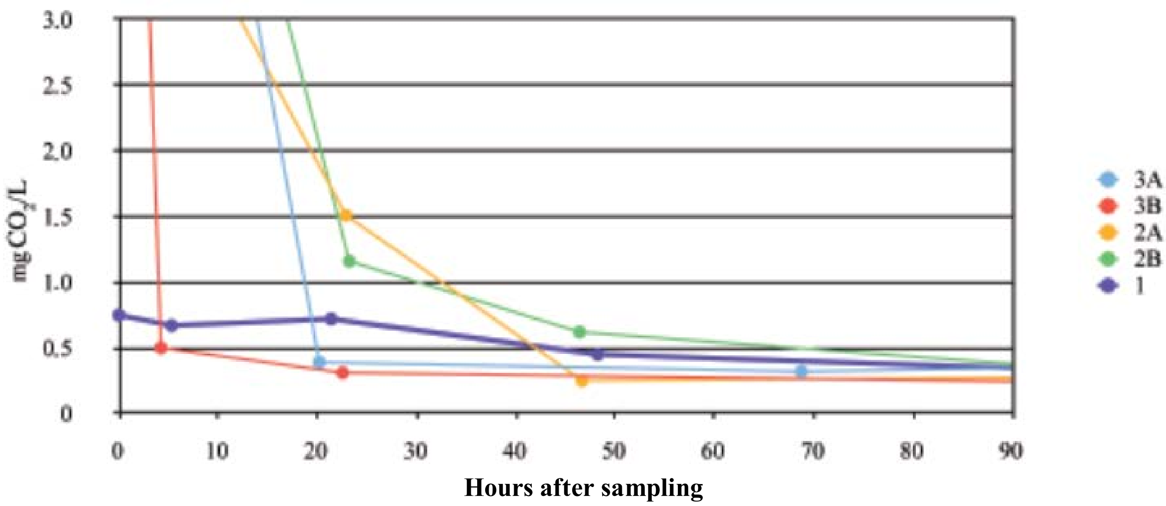

Fig. 6. Evolution of CO_2 content following permeate sampling, using a reduced scale.

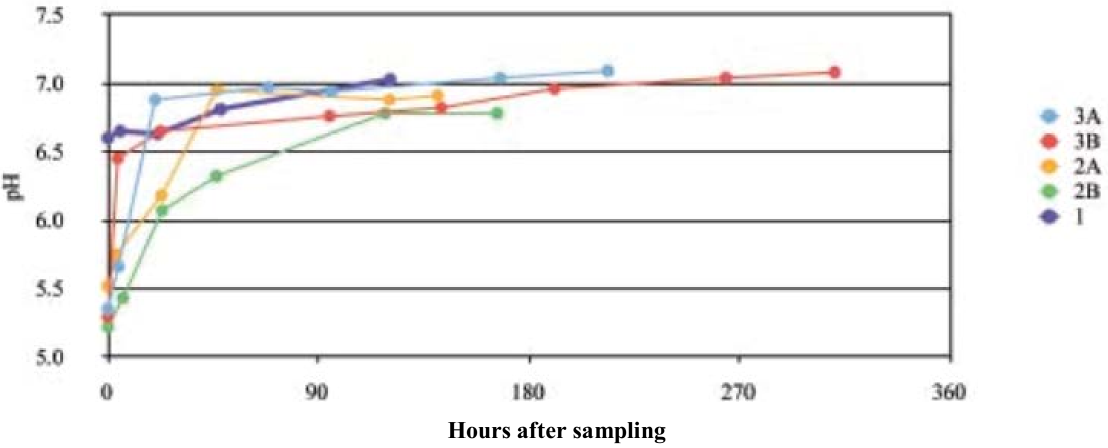

Fig. 7. Evolution of pH following permeate sampling.

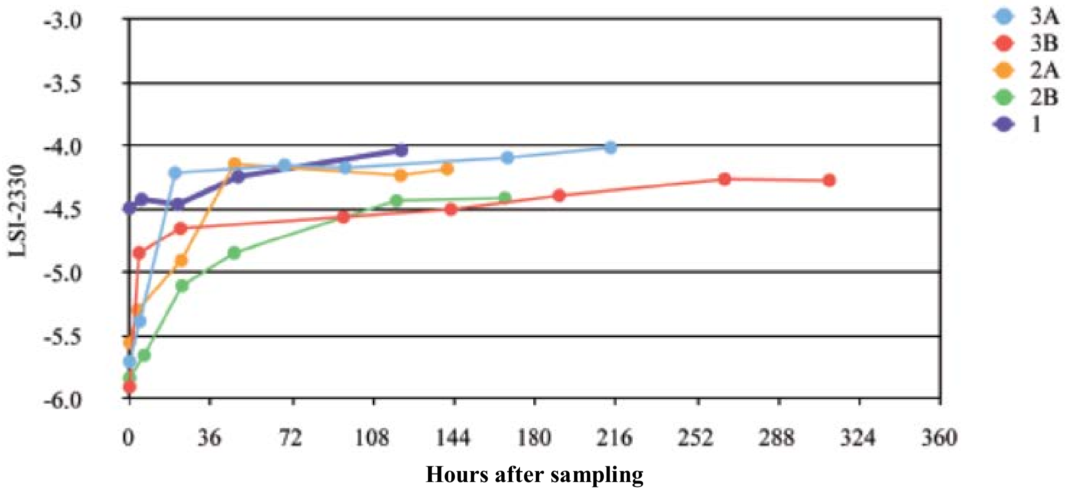

Fig. 8. Evolution of LSI-2330 following permeate sampling.

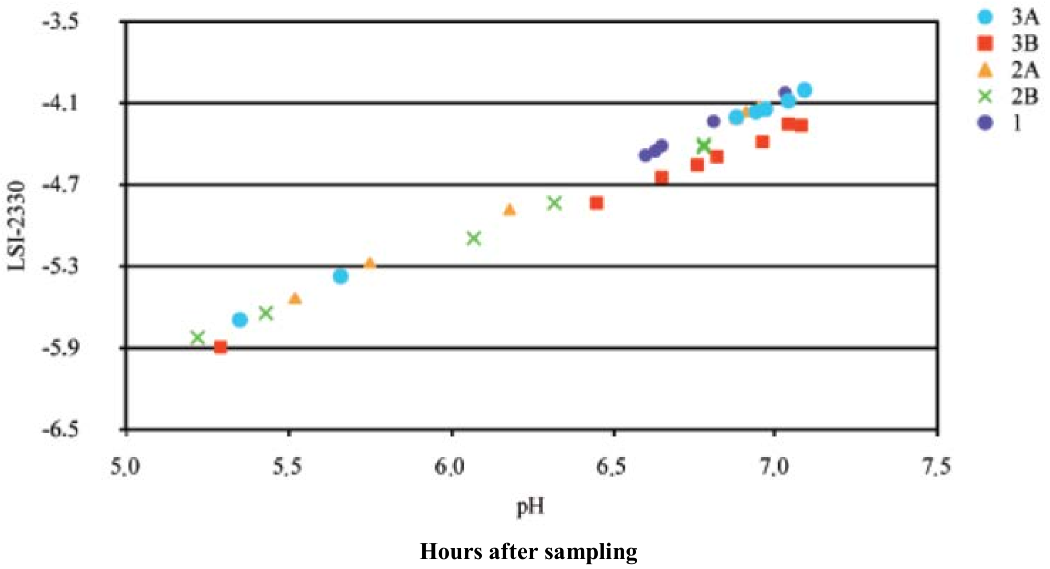

Fig. 9. Relationship between pH and LSI-2330 for permeated water.

usually indicative of corrosion problems in the facilities or defective membranes.

3.7. Larson–Skold Index

The Larson–Skold Index of desalinated water gives an average value of 152. This is indicative of water with an extreme tendency to produce pitting corrosion of unprotected iron or steel pipes.

3.8. Sodium adsorption ratio

The mean SAR of desalinated water is around 9. This points to water that can cause damage not only to the soil but also to some crops due to an excess of sodium over calcium and magnesium.

This aspect should therefore be corrected either with a remineralization or by adding calcium. and magnesium directly with fertilizers.

3.9. pH in balance with the calcite

Finally, in Table 1 the pH in equilibrium with the calcite is presented.

According to the data, none of the desalinated waters in Table 1 contains sufficient CO_2 at the outlet of the rack to complete a remineralization process adequately.

In any case, the CO_2 content of the desalinated water depends on the RO pre-treatment.

4. Conclusions

Desalinated water generally corresponds to a solution with a TDS content of around 280 mg/L of which 72% is ClNa. These are waters with very low bicarbonate content of around 2 mg/L as well as magnesium (2.4 mg/L) and calcium (1.4 mg/L). pH varies between 5.22 and 6.6 and CO_2 content between 0.75 and 16 mg/L.

In certain cases, where specific treatments are used to reduce boron content, the pH of the final permeate can exceed 8 and EC can be below 100 μS/cm. It is confirmed that the relationship between the pH of the desalinated water and the CO_2 content responds to criteria established in water chemistry.

The corrosivity indexes suggest that desalinated water tends to dissolve calcium carbonate and that, in view of its higher proportion of chlorine and sulphates with respect to bicarbonates, it is also corrosive in nature.

In some cases, the permeate immediately at the outlet of the pressure pipes has a certain CO_2 content that is lost in a few hours if it is in contact with the atmosphere.

Consequently, the pH of desalinated water depends to a large extent on the treatment to which the sample has been subjected prior to analysis. The CO_2 content of the desalinated water depends on the pre-treatment that the desalinated water has received.

Analyses indicate that the CO_2 content of desalinated water is often not sufficient to allow adequate remineralization without the addition of further CO_2. The turbidity of the desalinated water is around 0.2 NTU and higher values are indicative of problems in the facilities.

In balance with the atmosphere, the pH of the desalinated water is around 6.9 and 7.0 and the CO_2 content around 0.3 mg of CO_2/L. The Langelier index is around –4. The ratio between TDS and EC is around 0.47. The SAR of desalinated water is high, so it must be taken into consideration in order to avoid possible damage to soil structure or crops.

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