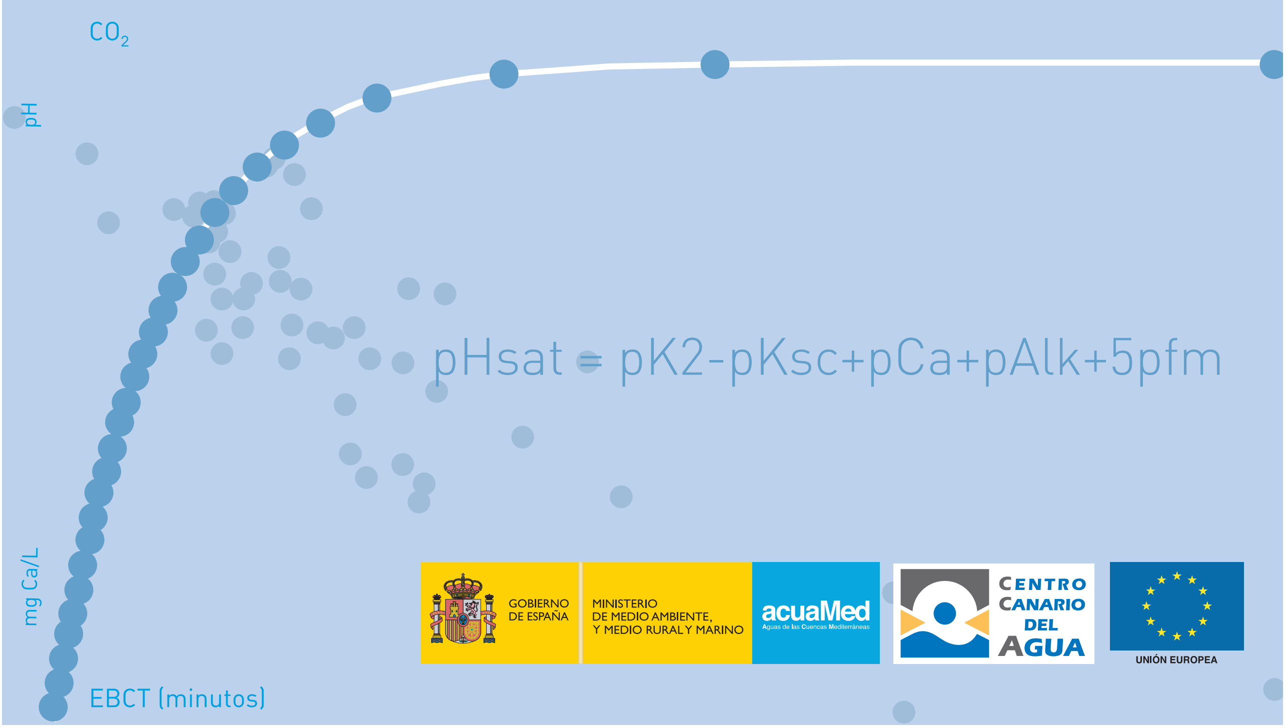
Manuel Hernández-Suárez

2ª edición
2nd edition

Guía para la remineralización de las aguas desaladas

Guideline for the remineralisation of desalinated waters



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First, thanks to Acuamed for publishing this Guide in my name and in that of the Canary Islands Water Center for giving me the opportunity to conduct this work.
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November 18th 2009

Explanatory note to the 2nd edition:

In January 2010 the first edition of the Guide was published. During its review it has been found that the method used in the laboratory for the analysis of the alkalinity of the permeated water could not determine it with a precision values lower than 5 mg $CaCO_3$*/L. Correction of this issue shows that the average value of the alkalinity of the permeated water that appear in Table 1.1 should be about 1.6 mg* $CaCO_3$ *instead of 6.6 mg* $CaCO_3$*.*
Corresponding the CO_2 *content calculated stoichiometrically from pH, temperature, electrical conductivity and alkalinity must be in the order of 8.5 mg* CO_2*/L instead of 36.1 mg* CO_2*/L as shown in Table 1.1.*
This inaccuracy in the analytical method only affects the values of alkalinity and CO_2 *content of permeated water but not remineralised water. Thus, only some figures and tables, especially Chapter 1, are affected.*
This inaccuracy, however, does not affect the water quality objective for remineralised water (Table 3.1) or to the proposed criteria for indirect calculation of the LSI (Chapter 4). Nor does it affect the evaluation criteria specified for remineralised water in the rest of the Guide.
This 2nd edition of the Guide now published correct this inaccuracy and broadens the criteria for indirect calculation of the LSI from the increase of the EC.

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PREFACE

Remineralisation, quality assurance for desalinated water

Since the desalination program of the Government of Spain began in April 2004, Acuamed has been committed to play a major role in the promotion of technological development, fostering collaboration with organizations and agencies that promote R&D projects, integrating them into the projects and disseminating information through national and international events and through publications, such as this one I have the privilege to present.

Acuamed work initially went to cover aspects related to the provision of new resources in the deficit territories. Once embarked on this objective, Acuamed has focused its efforts on research and preservation of the quality of desalinated seawater, beyond the standards and regulations. Ensuring a quality that preserves the integrity of materials and facilities, as well as suitability for different uses. This engagement is reflected in the work of this second edition of the Guide to Remineralisation of Desalinated Waters, sponsored by Acuamed.

I wish to express my appreciation to the author of this Guide, Manuel Hernández-Suárez, both for its clarity in the exposition of concepts regarding desalinated water assessment and its remineralisation and by the rigor in the development of a procedure for calculating indirectly the Langelier Saturation Index based on increases in electrical conductivity and alkalinity. A procedure and concept that, no doubt, will be implemented in many facilities.

The author's capacity of synthesis in the compilation of remineralisation techniques and the comparative analysis of remineralised and desalinated water makes it also a very useful document for all professionals working in the field of desalination.

Finally I wish to thank the institutional collaboration of the Canary Islands Water Center Foundation for their continued service and contribution to research and dissemination on water related issues.

Carlos Massa
General Manager of Acuamed

ÍNDICE

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0. SUMMARY AND CONCLUSIONS

OBJECTIVES

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

In particular, the specific objectives of the Guide are:

- *Establish the criteria for sampling and calculation of analytical results to define correctly the quality of desalinated and remineralized water;*
- *Establish what should be the optimal levels of remineralization within a reasonable cost;*
- *Establish an indirect method for evaluating the degree of remineralization through increases in pH and EC.*

SUMMARY OF WORK PERFORMED

In this Guide, "desalinated water" is defined as the water that comes directly from the reverse osmosis. Therefore "desalinated water" refers always to "non remineralised water". Desalinated water is also called permeate. It is important to note that the data handled for the preparation of this Guide come all from seawater desalination plants.

Work includes, first, an extensive bibliographical survey on these issues, with special attention paid to quality standards and analytical methods.

In parallel with the above, a series of analyses have been carried out on desalinated and remineralised waters from different desalination plants, in order to study their behaviour in contact with the atmosphere.

Following, the more frequent evaluation criteria, and especially the Langelier saturation index (LSI) and saturation pH calculation procedure (pHsat), where analysed.

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

In order to ensure optimum evaluation of the results, specific mathematical simulations were performed on water remineralisation and mixes, using scientifically sound calculation programmes.

An important part of the work has been oriented towards investigating changes in the composition of remineralised waters with respect to desalinated waters, with a view of developing a procedure for indirect calculation of the LSI and other indices on the basis of the increases in electrical conductivity (EC) and pH caused by remineralisation.

The Guide includes a summary of remineralisation techniques, with special emphasis on the calcite beds and lime slurry dosing techniques, including information to consider when dosing CO_2.

The Guide includes a section with instructions for sampling and analysis of desalinated and remineralised water considering their low alkalinity and the ease with which their CO_2 *content can change in contact with the atmosphere.*

Finally, the Guide includes a study with blending simulation programs and their usefulness for analysing the percentage of desalinated water that can be mixed with remineralised or hard inland waters.

CONCLUSIONS

The Guide consist of seven chapters. The following summarizes the major findings of each of them.

1. Characteristics of desalinated water

Desalinated waters are a solution with a mean content of 280 mg TDS/L and approximately 72% of ClNa. They have a very low content of HCO_3^- *(< 4 mg* HCO_3^-*/L) and* Ca^{2+} *(< 2.5 mg* Ca^{2+}*/L) and* Mg^{2+} *(< 4 mg* Mg^{2+}*/L).*

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 5.3 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 as a result of specific treatments. The 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 an LSI of less than -4, as a result of which it tends to dissolve calcium carbonate. It also implies the risk of problems of corrosion due to its higher chlorine (60-200 mg Cl^-*/L) and sulphate content (2-5.7 mg* $SO_4^=$*), 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, for which reason it should be analysed carefully and preferably "in situ".

In equilibrium with the atmosphere, the pH of osmotised 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 osmotised water is around 0.2 NTU, and higher values may be an indication of problems in the installations.

The SAR of osmotised water is equal to or higher than 9, this 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 the desalinated water generally does not contain sufficient CO_2 to permit adequate remineralisation without extra input of CO_2.

2. Desalinated and remineralised water evaluation criteria

Although there is a simplified method, also called ABCD method, for the calculation of pHsat that is frequently used as an indicator of the tendency of water to dissolve or precipitate calcium carbonate, it should be pointed out that this is an empirical method that does not consider a series of water chemistry aspects that should be taken into account in order to adequately assess those factors that intervene in the basic saturation reaction.

Consequently, this Guide recommends the use of the Standard Method 2330 (SM2330), based on a more rigourous calculation of the intervening reactions.

The two methods give different pHsat values. The value obtained using the simplified method is approximately 0.2 units lower than that obtained by SM2330.

Correspondingly, the LSI is also 0.2 units lower than that obtained by means of SM2330.

Bearing in mind that SM2330 is the internationally adopted method, it is considered that compliance with EU norm should be demonstrated in accordance with this standard method and not the simplified method.

3. Adequate levels of remineralisation

The purpose of remineralisation is generally to produce water with a Langelier index very close to zero that remains stable in contact with the atmosphere. Moreover, it is important accomplish this with a minimum consumption of CO_2 in order to minimise operating cost.

According to this study, it is considered that in order for desalinated water to be adequately remineralised, for a range of temperatures of between 14ºC and 25ºC it should present the characteristics shown in Table 0.1.

***TABLE 0.1:** RECOMMENDED CHARACTERISTICS FOR DESALINATED WATERS WITH AN ADEQUATE LEVEL OF REMINERALISATION.*

Parameter	*Range*
pH	*8.2 ± 0.1*
Alk, mg $CaCO_3$/L	*56 ± 3*
HCO_3^-, mg/L	*68 ± 3*
Ca^{2+}, mg/L	*21 ± 2*
CO_2, mg/L	*0.7 ± 0.1*
LSI (SM2330)	*± 0.15*

As indicated in Section 1, at most desalination plants, CO_2 needs to be added following inverse osmosis and prior to remineralisation to attain the values of Table 0.1.

The concentration of CO_2 in osmotised water necessary to reach the levels of remineralisation proposed in Table 0.1 depends on the permeate alkalinity prior remineralisation. Figure 0.1 shows the dose required for each water according to pH and alkalinity of the permeate prior to remineralisation with calcite beds.

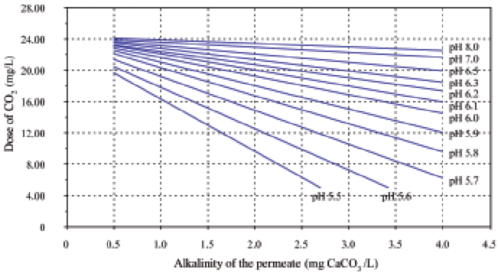

Figure 0.1: Relationship between alkalinity of the permeate and the dose of CO_2 required to obtain with calcite contactors a remineralised water with pH of 8.2 and 0.7 mg CO_2/L.

The dosage of Figure 0.1 refers to the remineralisation with calcite beds. In case of using $Ca(OH)_2$, the dosage of CO_2 should be doubled. Doses of Figure 0.1 are for a 100% efficiency, so it must be corrected upward if efficiencies lower (usually 80-95%).

Underdosing of CO_2 produces water with low alkalinity. This implies a low buffering capacity and therefore, a tendency to easily acidified by uptake of CO_2 from the atmosphere. This fact, coupled with the low calcium content, makes this type of water unstable, with a tendency to be corrosive.

Overdosing with CO_2 implies higher alkalinity and hardness in remineralised water, as well as a CO_2 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 since the remineralised water hardness does not usually reach 100 mg $CaCO_3$/L there is virtually no risk of precipitation of $CaCO_3$ while the LSI is between 0.5 and 1.0, even at temperatures of 40 ºC.

In many water networks LSI values between +0.1 to +0.5 are requested to protect the installations. This is achieved in the case of $CaCO_3$ postreatment by slightly increasing the pH by adding NaOH (2-4 mg NaOH/L). In the $Ca(OH)_2$ installations this is done with a slight overdose of $Ca(OH)_2$. In some occasions, technical limitations in controlling the exact dose of $Ca(OH)_2$ may cause an increase in turbidity above 1 NTU.

4. Indirect calculation of LSI and SAR on the basis of EC and pH data prior to and following remineralisation

The results obtained point to the possibility of calculating the LSI of remineralised water ($LSI_{(r)}$) on the basis of the increase in EC_{25} (EC at 25ºC) produced by remineralisation, using the quotient:

$\Delta EC_{25}/\Delta Alk$=1.55 - 1.75 (depending on the permeate EC_{25})

Where:

$\Delta Alk = Alk_{(r)} - Alk_{(o)}$, and
$\Delta EC_{25} = EC_{25(r)} - EC_{25(o)}$

Figure 0.2 presents the relationship between the permeate EC and the value of the ratio

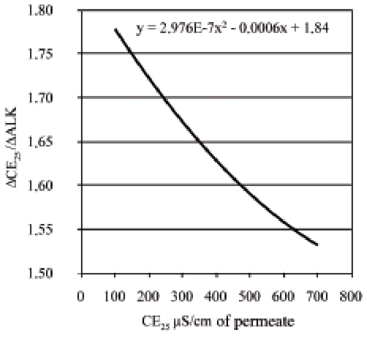

Figura 0.2: Relationship between the EC_{25} of the permeate and the ratio $\Delta CE_{25}/\Delta Alk$ for the water remineralised up to pH 8.2.

$Alk_{(o)}$ ranges from 0.5 to 2.8 mg $CaCO_3$/L for values of $EC_{25(o)}$ of between 250 µS/cm and 700 µS/cm respectively.

The $Ca_{(r)}$ value of remineralised water may be calculated from the ratio $Ca_{(r)} = Alk_{(r)}/2.5$.

The values of $pH_{(r)}$ and $T_{(r)}$ will be those acquired "in situ" with the measuring equipment placed in line.

Once all the parameters have been obtained, the $LSI_{(r)}$ calculation method should be SM2330.

This procedure allows $LSI_{(r)}$ to be estimated with an accuracy of ±0.05.

According to the study performed and in order to achieve the optimum levels indicated in Table 1, the increase in alkalinity should be at least 55 mg $CaCO_3$/L. This implies that the increase in EC should be within the range:

ΔEC_{25} = 85 - 97 µS/cm

The following may be assumed to calculate the $SAR_{(r)}$:

$Ca_{(r)} = Alk/2.5$
$Mg_{(r)}$ = 2.5 mg/L
$Na_{(r)}$ (mg/L) = 0.1549 x $EC_{25(0)}$ + 0.2137.

The sampling conditions should be optimized to prevent loss of CO_2 and obtain values of pH and temperature as close to operating conditions before and after remineralization system.

5. Remineralisation techniques

Analysis of the remineralisation techniques shows that the calcite bed and lime slurry techniques are both highly developed. The lower CO_2 consumption of the calcite bed technique and the lower degree of complexity of this process point to its being a more stable technique for the remineralisation of desalinated waters than dosing with lime slurry.

CO_2 dosage should be in down flow with a descending speed of about 0.07 ± 0.02 m/s in order to avoid dragging the bubbles or over dosage. The injection pressure should be about 0.25 bars greater than that of water.

The time required for the dissolution of CO_2 can be reduced considerably when using the criteria outlined in the preceding paragraph. Usually about 5 seconds are required for a dissolution of CO_2 from 10 to 40 mg / L using the above criteria.

In any case, the dosage of CO_2 in horizontal pipe should be avoided.

Decreases in temperature reduce the speed of the reactions intervening in remineralisation. In the case of calcite beds, the contact time required to achieve adequate remineralisation increases from 10 to 14 minutes with a decrease in water temperature from 28ºC to 14ºC.

6. Sampling techniques

The sampling of desalinated waters should be carried out in such a way that CO_2 *loss is avoided. For this reason, "in situ" measurements are recommended, especially of pH, temperature and EC.*

Taking note of the sampling conditions, along with the conditions in transport and during storage up to the moment of performance of the analyses facilitates interpretation of the results considerably.

The selection of appropriate method for analysis of alkalinity should be in line with the expected level of alkalinity of water. In not doing so can greatly overestimated the CO_2 *content, especially in the waters without remineralisation.*

7. Simulation of water blending

The blending simulation models coincide with an accuracy of 90%-95% with the results of the laboratory analyses.

The simulation points to the fact that if more than 15% of desalinated water is added to a remineralised water with an alkalinity of 60 mg $CaCO_3/L$*, the LSI will drop to below -0.5.*

The calculations performed using mixes of non-remineralised desalinated water and continental waters indicate that in certain cases up to 50% of desalinated water may be added without the LSI dropping to below -0.5.

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June 19th 2010

1. CHARACTERISTICS OF DESALINATED WATERS

1.1 Introduction

In Spain, practically all desalinated seawaters come from reverse osmosis plants. Consequently, whenever the term desalinated water is used in this Guide, the reference is to osmotised water from seawater desalination plants.

The composition of osmotised water varies depending on the type of plant and the way it operates. The addition of acids prior to osmosis varies the pH of the permeate and, therefore, its CO_2 content.

The condition of the membranes also affects the degree of salt rejection of the different components. Consequently, this also modifies the amount of total dissolved solids (TDS) and electrical conductivity (EC).

1.2 Materials and methods

For the study of desalinated waters samples were taken at different desalination plants and "in situ" analyses were performed of the pH, EC, Temperature, HCO_3^- and CO_3^{2+}.

The samples were then taken to the laboratory, where the analyses were repeated and completed for the rest of the parameters. Subsequently, the sample was left exposed to the atmosphere and agitated slightly using mechanical means, samples being taken for analysis every so often over a period of 14 days.

***TABLE 1.1:** AVERAGE COMPOSITION OF DESALINATED WATERS FROM SIX DESALINATION PLANTS UNDER NORMAL OPERATING CONDITIONS. PH, CE, HCO_3^-, CO_3^{2-} AND TEMPERATURE ANALYSED "IN SITU". OTHER PARAMETERS ANALYSED IN THE LABORATORY. AVERAGE VALUES FOR EACH DESALINATION PLANT.*

	Plant 1	Plant 2A	Plant 2B	Plant 3A	Plant 3B	Plant 4	AVERAGE	STD	Sea water[10,11,12]
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	oct and nov 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
CE_{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^a, ºC	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_{180}, mg/L		274	97	340	172		220.65	107.56	
RS_{180}/CE_{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}/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 $CaCO_3$	9.79	9.08	8.76	8.62	8.90	9.35	9.08	0.40	

**) The value of HCO_3^- has been estimated from the EC and the RO membranes specifications since the method used in the laboratory did not permit a precise determination of alkalinity values < 6 mg HCO_3^-/L.*

†) The CO_2 has been calculated from the values of TDS, HCO_3^-, pH and temperature.

TABLE 1.1B: *GENERAL CHARACTERISTICS OF THE DESALINATION PLANTS INCLUDED IN TABLE 1.1.*

	Planta 1	Planta 2A	Planta 2B	Planta 3A	Planta 3B	Planta 4	Planta 5	Planta 6
Date of start-up	Oct. 2002	Sept. 2003	Aug. 2007	Jan. 2007	Nov. 2006	Feb. 2003	Membrane programme simulation	Feb. 2008
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 waters. Mediterranean	Coastal drains mixed with fossil saline waters. 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

1.3 Results and discussion

The variation in the composition of desalinated waters from various desalination plants is illustrated by the results shown in Table 1.1. These results have been extracted from the data analysed and reflect a range of values frequently provided by osmosis plants. The characteristics of the desalination plants in question are shown in Table 1.1B.

Table 1.1 shows the average values of the samples taken from six desalination plants and analysed "in situ": i.e. at the moment of sampling. Given that these are samples taken "in situ" and carefully analysed in order to prevent losses of CO_2, they may be assumed to reflect the average quality of the water at the outlet of the rack.

Table 1.2 shows the data from another two desalination plants at which the pH of the permeate was increased upstream of the rack in order to increase boron rejection at the membranes. These waters have a pH higher than 8 and at times of up to 10 (plant 5). However, they conserve the rest of the characteristics typical of desalinated waters, that is to say a TDS < 300 mg/L with 72% of sodium chloride.

Table 1.1 reflects a certain variation in EC. This variation is related to specific situations in the process, for example in the case of Plant 2B, where the yield of the membranes is abnormally high, or as it happen in Plant 5 due to the existence of a second step.

The normal value of EC in straightforward single-step desalinating plants is between 500 - 700 µS/cm. In two-step plants, a part of the permeate is desalinated a second time and mixed subsequently at the outlet. In these cases the EC oscillated between 80 and 400 µS/cm.

In any case, the quality of osmotised water depends on several factors, such as physical/chemical pre-treatment, the temperature of the water and the chemical composition of the raw water. Consequently, each particular case requires a detailed study that is beyond the scope of this Guide.

Detailed information on the quality of seawater, desalination systems and their relation to the quality of desalinated water may be found in the specific literature. [1,2,3,4,5]

TABLE 1.2: *AVERAGE COMPOSITION OF DESALINATED WATERS FROM 2 DESALINATION PLANTS IN WHICH THE pH HAS BEEN INCREASED IN ORDER TO INCREASE BORON REJECTION BY THE RO MEMBRANES.*

	Plant 5	Plant 6
DATE	02-07-09	04-06-09
pH	10.0	8.6
CE_{25}, µS/cm	50	624
HCO_3^-, (mg/L)*	0.1	1.2
CO_3^{2-}, (mg/L)	0.01	0.01
T^a, ºC	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

**) The value of HCO_3^- has been estimated from the EC and the RO membranes specifications since the method used in the laboratory does not permit a precise determination of alkalinity values < 6 mg HCO_3^-/L.*
†) The CO_2 has been calculated from the values of TDS, HCO_3^-, pH and temperature.

1.3.1 Relationship between CO_2 and pH in desalinated waters

Table 1.1 shows the variation in pH at the plants, which as may be appreciated varies between 6.6 and 5.27. Correspondingly, CO_2 content varies between 0.75 mg CO_2/L and 16 mg CO_2/L. The data reflect the relationship that exists between CO_2 and pH. Figure 1.1 shows the results obtained, underlining the clear relationship between the two parameters.

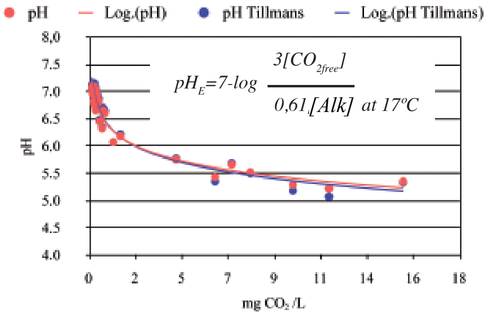

Figure 1.1: Relationship between CO_2 content and pH in desalinated waters according to data analised in the laboratory and those calculated with the Tillmans ratio.[7]

This ratio practically corresponds to the formula presented by Tillmans[7] and published in 1912 and where the concentration of CO_2 and alkalinity are expressed in mg/L.

1.3.2 Relationship between EC and the presence of Cl and Na

Desalinated water is a solution with around 72% of ClNa. Thus, the conductivity of desalinated water increases proportionally with increasing Cl and Na. Figure 1.2 shows this relationship. The ratio between Cl^- and Na^+ is 1.25 mMol Cl^- per mMol Na^+, as shown in Figure 1.3.

1.3.3 Ca^{2+} and Mg^{2+} contents

The contents in Ca^{2+} and Mg^{2+} maintain a certain proportionality, as is reflected in Figure 1.4. In accordance with these data, it may be assumed approximately that
Mg^{2+} (mg/L) = 1,7 x Ca^{2+} (mg/L).

However, with the data available no clear relationship has been found between EC and
Ca^{2+} and Mg^{2+} contents.

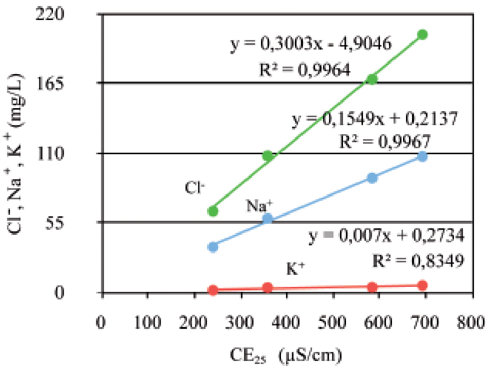

Figure 1.2: Relationship between EC and Cl^-, Na^+ and K^+ contents. Data from Table 1.1.

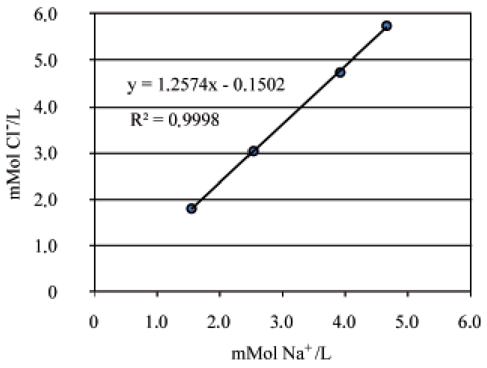

Figure 1.3: Relationship between mMol of Cl^- and mMol of Na^+ according to data from Table 1.1.

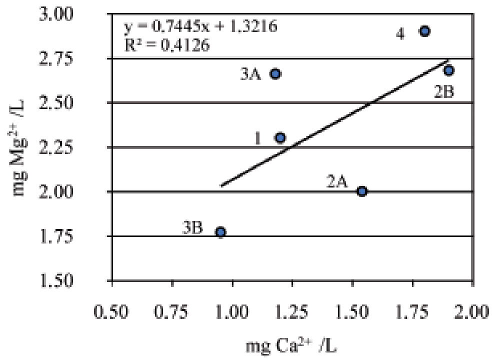

Figure 1.4: Relationship between Ca^{2+} and Mg^{2+} according to data from Table 1.1.

1.3.4 Behaviour of desalinated water in contact with the atmosphere

The sensitivity of desalinated water to sampling quality is underlined by the results shown in Figures 1.5, 1.6 and 1.7. According to these results, desalinated waters tend to equilibrate with the CO^2 in the atmosphere in a few hours. This *requires great caution when interpreting permeate samples since the pH may be affected significantly in just 2 hours.*

Figure 1.6 shows that desalinated water in equilibrium with the atmosphere contains around 0.3 mg CO_2/L. This value contrasts with the value of 0.6-0.7 mg CO_2/L for remineralised waters. The difference is due to the different pH in equilibrium with the atmosphere for both types of waters. (See Chapter 4 on the characteristics of remineralised waters).

As may be deduced from Figures 1.5, 1.6 and 1.7, the decrease in CO_2 content is very fast and is related to the low alkalinity of desalinated waters (see Chapter 2 for more information on the assessment of alkalinity of osmotised water).

Figure 1.8 illustrates the evolution of LSI[8] over time for the same data as in Figure 1.5. As may be observed, the LSI stays at around -4 even after 10 days of exposure of the water to the atmosphere. The negative value of the LSI points to the fact that desalinated water maintains the tendency to dissolve calcium carbonate in an open system.

Figure 1.9, for its part, illustrates the relationship between pH and LSI using the data of Figures 1.7 and 1.8. A clear relationship can be observed between the two parameters. Further details on calculation of the Langelier Saturation Index (LSI) and its meaning may be obtained from Chapter 2 of this Guide.

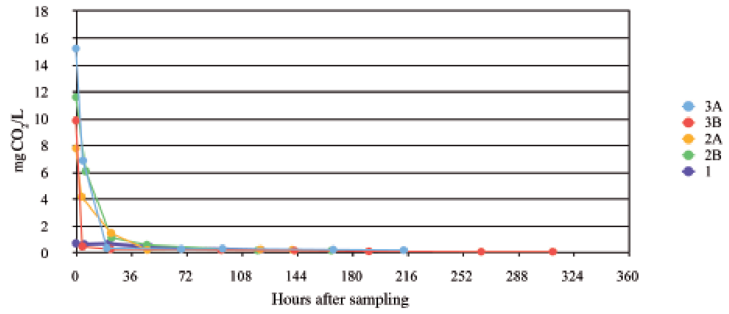

Figure 1.5: Evolution of CO_2 contents following sampling for permeated water. *The samples were kept exposed to the atmosphere and gently slightly in the laboratory following sampling.*

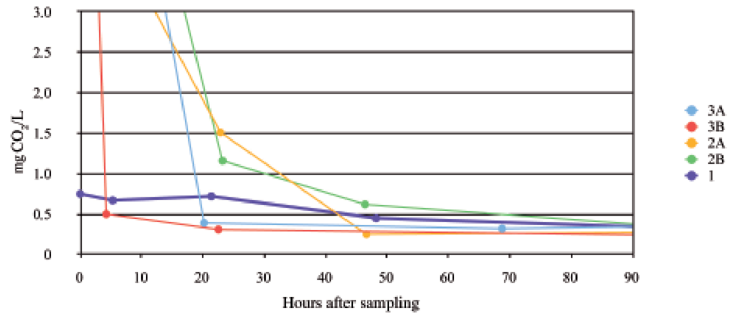

Figure 1.6: Evolution of CO_2 contents following sampling for permeated water. *These are the same data as in Figure 1.5 but with the CO_2 scale reduced. The samples were kept exposed to the atmosphere and softly stirred in the laboratory following sampling.*

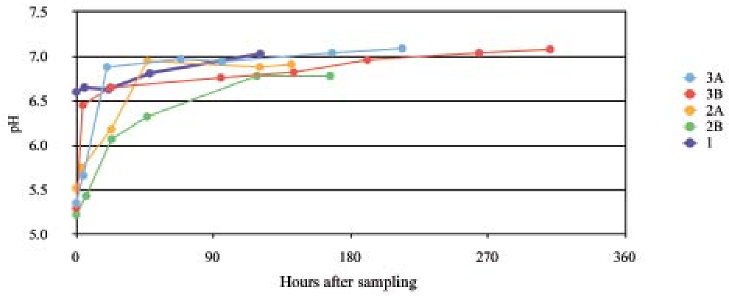

Figure 1.7: Evolution of CO_2 contents following sampling for permeated water. *The samples were kept exposed to the atmosphere and softly stirred in the laboratory following sampling.*

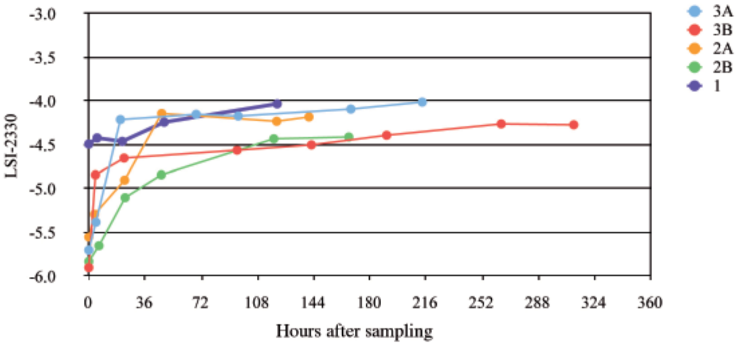

Figure 1.8: Relationship between pH and LSI-2330 for permeated water.

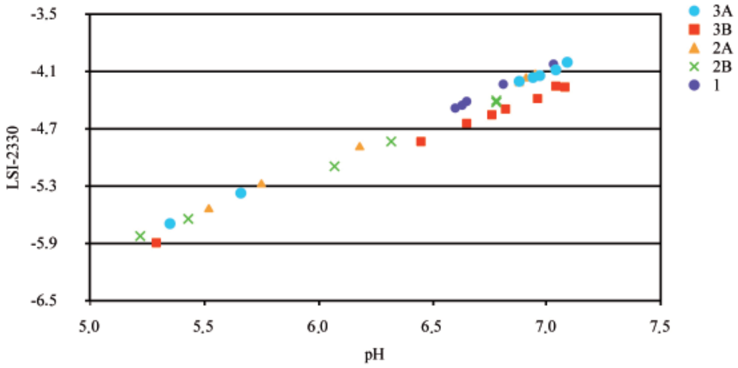

Figure 1.9: Relationship between pH and LSI-2330 for permeated water.

1.3.5 Total dissolved solids (TDS)

As is shown in Table 1.1, the values of TDS vary slightly depending on the method used to obtain them. As can be seen the difference between the average values obtained by both methods is only 1 mg/L and, therefore, less than 1%. It is considered, however, that the sum method of anions and cations is considered more accurate because the method by drying at 180 º C can cause small errores.[9]

In any case, the value of the STD has little effect on the calculation of the LSI-2330 (see Chapter 2, Section 2.4.5) and selecting a value between 0.47 and 0.46 does not produce any significant difference.

1.3.6 Turbidity of desalinated water

The turbidity of osmotised waters is low, around 0.2 NTU. Higher values of turbidity are usually indicative of corrosion problems in the installations or of defective membranes.

1.3.7 Larson-Skold index

The Larson-Skold index[13] *of desalinated water shows an average value of 151. This is indicative of a water clearly tending to cause pitting in unprotected iron or steel piping. Chapter 2 of this Guide includes further information on the Larson-Skold index and its interpretation.*

1.3.8 SAR

The average value of the SAR[14] *or sodium adsorption ratio is around 9. This points to a water that may cause important damage not only to the soil but also to certain crops, due to an excess of sodium with respect to calcium and magnesium. For this reason it is convenient to remineralise or to add Ca and Mg directly with fertilisers. For more information on the SAR, refer to Chapter 2 of this Guide.*

1.3.9 pH in equilibrium with calcite

Finally, Table 1.1 shows also the pH in equilibrium with calcite. According to these data and as discussed below along this Guide, none of the desalted waters of Table 1.1 contain enough CO_2 *at the racks outlet to complete a remineralization process properly. In any case, the* CO_2 *content of osmotic water depends on the pretreatment of the R.O.*[1,2]

1.4 Conclusions

Desalinated waters consist of a solution with a TDS content of around 280 mg/L and a ClNa content of approximately 72%. They are waters that have a very low content of HCO_3^- *(≈ 2 mg* HCO_3^-*/L,) as well as* Mg^{2+} *(2.4 mg/L) and* Ca^{2+} *(1.4 mg/L). The* Mg^{2+} *and* Ca^{2+} *contents are proportional, with something of a relationship between both: mg* Mg^{2+}*/L ≈ 1.7 x mg* Ca^{2+}*/L.*

The pH ranges from 5.3 to 6.6 and CO_2 *content from 0.75 to 16 mg* CO_2*/L, although certain waters may provide values outside this range.*[6]

In certain cases, where specific treatments are used to reduce boron content, the pH of osmotised water may exceed a value of 8 and the conductivity below 100 µS/cm.

It is confirmed that the relationship between the pH of osmotised water and CO_2 *content rests on criteria established in water chemistry.*[7]

The corrosivity indexes suggest that osmotised 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 certain cases the waters at the outlet of the reverse osmosis tubes contain important amounts of CO_2 *that are lost in a few hours if the water 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 turbidity of osmotised water is around 0.2 NTU, with higher values considered to be an indicator of problems in the installations.

In equilibrium with the atmosphere, the pH of osmotised water is around 6.9 – 7.0 and CO_2 *content around 0.3 mg* CO_2*/L. The LSI remains at around -4.*

The TDS/EC_{25} *quotient has a value around 0.47.*

The SAR of osmotised water is high and should be kept in mind to avoid possible damages to soil structure and crops.

1.5 References

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2. CRITERIA FOR THE ASSESSMENT OF DESALINATED AND REMINERALISED WATERS

2.1 Introduction

The quality criteria used in practice to evaluate continenal waters are applicable also in the assessment of desalinated and remineralised waters.

This chapter summarises the most important criteria in accordance with the works published in the literature[1 to 13] *and analyses their applicability to desalinated and remineralised waters on the basis of data from operating plants.*

2.2 Materials and methods

Firstly, a literature review was performed on the evaluation of corrosive waters proportionally rich in sodium chloride. Furthermore, data were collected from different desalination plants and distribution reservoirs to analyse the suitability of the different assessment criteria and the need to adapt the empirical correlation parameters used in some corrosion indexes to the characteristics of desalinated and remineralised waters.

2.3 Hardness

Originally, the hardness of water was understood as being a measurement of its capacity to precipitate soap. It was later discovered that soap precipitated due to the presence of calcium and magnesium in the water.

Other polyvalent cations may also precipitate soap, although they are generally present in complex form. They are frequently organic compounds and their role in regards to water hardness is usually minimal and difficult to define. In the case of desalinated and remineralised waters these cations are not included in hardness calculation.

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

$$mg\ CaCO_3/L = 2.497\ [Ca^{2+}, mg/L] + 4.118\ [Mg^{2+}, mg/L]$$

When the milligrams of $CaCO_3$ of hardness exceed the milligrams of $CaCO_3$ of alkalinity, the milligrams of $CaCO_3$ defined by alkalinity are understood to refer to carbonated hardness and the rest to non-carbonated hardness. As may be appreciated in Tables 2.1 and 2.2, the total hardness of desalinated and remineralised 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.

When the hardness is equal to or, lower, than alkalinity, all the hardness is carbonated, and non-carbonated hardness disappears. Table 2.3 includes a type assessment scale.[9]

TABLE 2.1: *HARDNESS AND ALKALINITY OF DESALINATED WATERS, IN MG $CaCO_3$/L.*

	Plant 1	Plant 2A	Plant 2B	Plant 3A	Plant 3B	Plant 4	Avg.
TH	12.47	12.08	15.78	13.90	9.66	16.44	13.41
Alk	1.61	1.21	0.67	1.61	0.90	1.97	1.33

TABLE 2.2: *HARDNESS AND ALKALINITY OF REMINERALISED WATERS, IN MG $CaCO_3$/L.*

	Plant 1	Plant 2A	Plant 2B	Plant 3A	Plant 3B	Plant 4	Avg.
TH	60.51	56.58	72.67	44.10	46.91	34.69	52.58
Alk	46.00	49.38	60.00	36.25	38.75	17.83	41.37

TABLE 2.3: *TABLE FOR THE ASSESSMENT OF THE HARDNESS OF WATER IN MG $CaCO_3$/L.*[1]

Hardness (mg $CaCO_3$/L)	Assessment
< 17.1	soft
17.1 - 60	slightly hard
60 - 120	moderately hard
120 - 180	hard
> 180	very hard

Table 2.1 shows the values of hardness and alkalinity of desalinated waters. According to these criteria, the waters in question are soft, with a hardness of around 12 mg $CaCO_3$/L, 70% to 75% of which is due to magnesium.

In remineralised waters (Table 2.2), hardness shows an average value of 52.58 CaC_3/L, this indicating that the water is slightly hard. In this case the contribution made by magnesium to hardness amounts to only 14-18%.

Hardness is expressed in different ways depending on the country in question. Table 2.4 includes the equivalent values.

TABLE 2.4: EQUIVALENCE BETWEEN DIFFERENT EXPRESSIONS OF HARDNESS

Hardness	Value
mg $CaCO_3/L$	10
mg Ca^{+2}/L	4
mg HCO_3^-/L	12.2
º French	1.00
º German	0.56
º English	0.70

2.4 Alkalinity

Alkalinity (Alk) is defined as the capacity of the components of an aqueous solution to neutralise acids. Like hardness it is expressed in mg $CaCO_3/L$. In desalinated and remineralised waters it relates to the presence of bicarbonates and carbonates.

At pH values higher than 8.3, carbonates and hydroxides also contribute to alkalinity. This may occur especially with treatments based on $Ca(OH)_2$ and CO_2 by infra-dosing CO_2.

The reader is referred to specific literature[1,2,7,8,17] for more information on alkalinity measurement techniques.

Table 2.5 summarises the alkalinity assessment criteria.

TABLE 2.5: TABLE FOR THE ASSESSMENT OF THE ALKALINITY OF WATERS IN MG CaCO/L

Alkalinity (Alk) (mg $CaCO_3/L$)	Assessment
< 12.3	very low
24.6 - 41	low
41 - 98.4	medium
98.4 - 147.6	high
> 147.6	very high

2.5. Saturation or Langelier index

Wilfred F. Langelier[3] was one of the first scientist to investigate which value of pH would make it possible to guarantee that $CaCO_3$ would not precipitate or dissolve in water.

He established the following reaction as a basis:

$$CaCO_3(s) + H+ = Ca^{2+} + HCO_3^- \qquad [1]$$

and postulated that in order for the concentration of $CaCO_3(s)$ to remain constant a situation of equality would need to be fulfilled:

$$kCaCO_3 = [Ca^{2+}][HCO_3^-]/[H^+]$$

Extracting logarithms and solving:

$$pHsat = pCa^{2+} + pHCO_3^- \, pKCaCO_3 \qquad [2]$$

Where:

pHsat: saturation pH is, therefore, the theoretical value at which the solution would be saturated with calcite under conditions of chemical equilibrium in which the calcite neither dissolves nor precipitates. Under these conditions of equilibrium there are no changes in alkalinity, calcium content or dissolved solids.

pCa^{2+}: negative logarithm of Ca^{2+} concentration expressed in mg $CaCO_3/L$. (1 mg Ca^{2+}/L = 2.497 mg $CaCO_3/L$).

pAlk: negative logarithm of alkalinity to methyl orange expressed in mg $CaCO_3/L$. As regards to alkalinity measured using heliantine or methyl orange, shift is performed at a pH of approximately 4.3 and corresponds to all the carbonates and bicarbonates.[1]

It is accepted that if pH<9 all alkalinity is due to bicarbonates and 1 mg HCO_3^-/L= 1.22 mg $CaCO_3/L$.

$$pKCaCO_3 = pK_2 - pKsc$$

where :

pK_2: negative logarithm of the constant of ionisation of HCO_3^-
pKsc= negative logarithm of the product of solubility of $CaCO_3$

The term pK_2-pKsc depends on ionic force and on temperature.

In accordance with these terms, Langelier established the following formula for pHsat:

$$pHsat = pCa^{2+} + pAlk + (pK_2 - pKsc)$$

establishing the saturation index as:

$$LSI = pH - pHsat$$

Initially the saturation index was known as SI but with time the industry identified it with the work of Langelier and changed the name to Langelier Saturation Index or LSI.[9]

Originally Langelier developed a series of nomograms for the calculation of pHsat that have subsequently been improved and adapted to include the concepts of temperature and ionic force.[4]

Figure 1.1 shows a typical diagram for the simplified calculation of pHsat.[5]

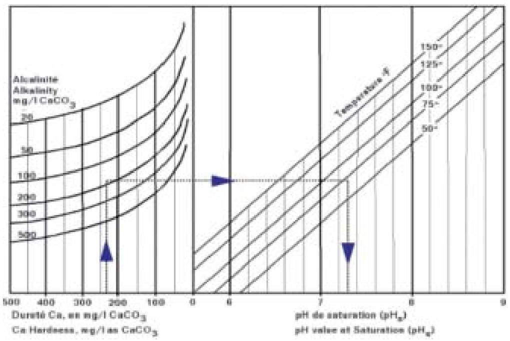

Figure 1.1: Nomogram for the simplified calculation of LSI. ºF = (ºC x 9/5)+32.[5]

Subsequently, on the basis of the work of Larson and Buswell[5] *and of Langelier himself*[4]*, a numerical model was developed based on practical data that facilitated calculation considerably.*

2.5.1 Simplified method for the calculation of pHsat

In response to the demand for a numerical procedure for the calculation of pHsat, and in accordance with the work of Larson and Buswell[6]*, a simplified empirical formula has been developed for the calculation of pHsat, this becoming widespread because of its simplicity. This formula is as follows:*

$pHsat = (9.3 + A + B) - (C + D)$

Where:

$A = 1/10\ (\log(TDS)-1)$
$B = -13.12 \times \log(T(^{o}C)+273.2)+34.55$
$C = \log(Ca(mgCaCO_3/L))-0.4$
$D = \log Alk(mg\ CaCO_3/L)$

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 [1].

Consequently, this Guide recommends the use of the standard method SM2330 described in the following paragraph, based on a more rigorous calculation of the reactions intervening.

These two methods differ as regards the value of pHsat, the LSI obtained using the simplified method being approximately 0.2 units lower than that obtained with SM2330.

The simplified LSI calculation method is available at www.fcca.es => Software (free of charge).

2.5.2 SM2330 method for the calculation of pHsat

The standard SM2330[1] *method summarises the progress made to date in water chemistry and is the internationally accepted method for the calculation of pHsat.*

The SM2330[1] *method is a more accurate and precise model that includes thermodynamic concepts of reaction [1].*

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

$pHsat = pK_2 + pKsc + pCa^2 + pAlk + 5pfm$

Where:

K_2 = *Second constant of disassociation for carbonic acid at water temperature.*
Ksc = *Product of solubility for calcite at water temperature.*
Ca^{2+} = *Calcium, in mols-g/L*
Alk = *Alkalinity, in equivalents-g/l.*
pfm = *Coefficient of activity at the specified temperature.*

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

$pK_2=107.8871+0.03252849T-5151,79/T-38,92561\ \log10T+563713.9/T2$, *for a temperature range of 273-373 ºK*
$pKsc=171.9065+0,077993T-2839.319/T-71,595\log10T$, *for a temperature range of 273-363 ºK*
$pfm = A(I\text{^}0.5/(1+I\text{^}0.5))-0.31$, *valid for* $I< 0.5$

Where:

$I = 1.6 \times 10-5 \times CE_{25}$
$A = 1.82 \times 106\ (E\cdot T)-1.5$
$E = [60954/(T+116)]-68.937$

Where:

I= *Ionic strength*
EC_{25}= *Electrical conductivity, µmhos/cm or µS/cm*
T= *Temperature of water, ºK (ºC + 273.2)*
E = *Dielectric constant*

The LSI calculation method according to SM2330 is available at www.fcca.es => Software (free of charge).

2.5.3 Calculation factor for ionic strength (I)

In accordance with SM2330, calculation of the ionic strength "I" may be performed on the basis of conductivity and in accordance with empirical data obtained from continental waters.

In view of the specific characteristics of desalinated and remineralised waters, this coefficient has been revised using the method for the calculation of activity "A" from the ion conductance of each of the cations and anions, this being the system proposed as an alternative in SM2330.[1]

According to these estimates the correct value would be $1.07 \times 10^{-5} \times CE_{25}$ instead of $1.6 \times 10^{-5} \times CE_{25}$.

This difference implies that the SM2330 calculated with the value of $I = 1.6 \times 10^{-5} \times CE_{25}$ is between 0.03 and 0.04 more negative than that obtained with the value $I = 1.07 \times 10^{-5} \times CE_{25}$.

However, considering this difference is small and in order not to hinder the use of existing calculation programs the value for I given in the SM2330 is used along this Guide.

2.5.4 Comparison of calculation of LSI using the simplified method and SM2330

In view of the fact that both methods are used in practice, it would be advisable to look at the difference between the simplified LSI and the LSI given by SM2330. The analysis of these differences for desalinated and remineralised waters is shown in Tables 2.6 and 2.7 respectively. According to these data there is a difference of 0.2 points between the two calculation methods, regardless of whether the reference is to desalinated or remineralised waters.

TABLE 2.6: COMPARATIVE ANALYSIS BETWEEN CALCULATION OF LSI BY THE SIMPLIFIED METHOD AND BY SM2330 FOR DESALINATED WATERS.

	Plant 1	Plant 2A	Plant 2B	Plant 3A	Plant 3B	Plant 4
LSI (simplified)	-4.35	-5.07	-5.365	-5.32	-5.59	-4.71
LSI (SM2330)	-4.17	-4.86	-5.135	-5.14	-5.37	-4.53
Difference	-0.18	-0.21	-0.23	-0.18	-0.22	-0.18

TABLE 2.7: COMPARATIVE ANALYSIS BETWEEN CALCULATION OF LSI BY THE SIMPLIFIED METHOD AND BY SM2330 FOR REMINERALISED WATERS.

	Plant 1	Plant 2A	Plant 2B	Plant 3A	Plant 3B	Plant 4
LSI (simplified)	-0.30	-0.80	-0.32	-0.60	-0.42	-0.62
LSI (SM2330)	-0.13	-0.60	-0.09	-0.40	-0.20	-0.45
Difference	-0.17	-0.20	-0.23	-0.20	-0.22	-0.17

2.5.5 Value of TDS

The simplified LSI uses TDS instead of EC_{25} (this is allowed also by SM2330), consequently this may be considered important.

Table 2.8 shows the average values for desalinated and remineralised waters of four of the plants studied. A value of 0.6 is considered to be suitable in both cases.

The sum of anions and cations has been used instead of the drying at 180^{o} procedure to obtain the values of TDS, since this method may be considered more reliable.[11]

Furthermore, LSI analysis using the simplified method with TDS values of 0.47 or 0.56 shows that LSI does not vary, or does so by only 0.01 units.

2.6 PHsat and pHeq

TABLE 2.8: VALUE OF THE QUOTIENT TDS/EC_{25} FOR DIFFERENT DESALINATION PLANTS

	Plant 2A	Plant 2B	Plant 3A	Plant 3B	Avg.
STD/CE_{25} desalinated	0.47	0.49	0.47	0.47	0.47
STD/CE_{25} remineralised	0.54	0.61	0.50	0.57	0.56

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

$$CaCO_3(s) + CO_2(aq) + H_2O \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^{-}(aq)$$

The equilibrium pH is obtained from analysis of the acid-base chemistry and in accordance with the Henderson-Hasselbalch formula.[12]

Consequently, pHeq does not depend on whether or not 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 LSI is equal to zero.

Figures 3.3, 3.4 and 3.5 in Chapter 3 illustrate the difference between pHeq and pHsat.

2.7 Effect of temperature on LSI

The LSI is affected by water temperature as shown in Figure 3.12 of Chapter 13 for remineralised water with different levels of alkalinity.

2.8 LSI in the Spanish legislation

Royal Decree 140/2003, Annex 1, Table C: Distribution network Indicating Parameters, establishes that "at no time may the water be aggressive or scale-forming and the result of calculating the Langelier index should be +/- 0.5".

Although RD 140/2003 does not specify whether the simplified method or SM2330 should be used, it is understood that the official method should be SM2330.

2.9 Larson-Skold index

This is similar to the DIN 50930 standard (see below) and is also indicative of the pitting potential. The Larson-Skold[13] *index is calculated as follows:*

$LaI = ([Cl^-] + [SO_4^{2-}])/([HCO_3^-] + [CO_3^{2-}])$

Where the assessment criteria are as follows:

$LaI > 1.2$	*High degree of corrosion*
$0.8 < LaI < 1.2$	*Significant degree of corrosion*
$LaI < 0.8$	*No risk of corrosion*

2.10 DIN standards

There are a number of German industrial DIN standards that develop criteria similar to SM2330 and the Larson-Skold index. These are DIN 4046 and DIN EN 12502, which refer to the capacity of water to dissolve calcite and to the risks of corrosion for different materials. On the other hand, DIN 50930, which refers to the risk of corrosion due to pitting and is similar to the Larson-Skold index. At international level DIN 50930 is applied in certain cases. This standard establishes the value of "S" as follows:

$S = ([Cl^-] + 2[SO_4^{2-}])/[HCO_3^-]$

and recommends S<1 to minimise the risk of corrosion due to pitting.

2.11 Ryznar index

This is an empirical index14 that was developed for continental waters and that does not really provide any additional information for desalinated or remineralised waters.[14]

$RSI = 2(pHsat) - pH$

The assessment criteria are as follows:

$RSI > 9.0$	*Unacceptably corrosive*
$7.5 < RSI < 9.0$	*Strongly corrosive*
$7.0 < RSI < 7.5$	*Significantly corrosive*
$6.0 < RSI < 7.0$	*Slightly scale-forming or corrosive*
$5.0 < RSI < 6.0$	*Slightly scale-forming*
$4.0 < RSI < 5.0$	*Strongly scale-forming*

2.12 Puckorius index

This is an empirical index[15] *obtained from continental waters, similar to the Ryznar index, but in which pH is replaced with a pH related to alkalinity. It does not provide any additional information in the case of desalinated and remineralised waters.*

$PSI = 2(pHsat) - pHpuckorius$

Where:

$pHpuckorius = 1.465 \times Log [Alkalinity] + 4.54$

The assessment criteria are as follows:

$PSI > 6.5$	*Tendency to corrosion*
$4.5 < PSI < 6.5$	*Optimum range*
$PSI < 4.5$	*Tendency to scaling*

2.13 SAR

The SAR (Sodium Adsorption Ratio)[16] *of the water is as reflected in the following formula:*

$SAR = Na^+/((Ca^{2+} + Mg^{2+})/2)^{0.5}$

Where Na^+, Ca^{2+} and Mg^{2+} are expressed in meq/L.

And where the assessment criteria are as follows:

$SAR > 12$	*Very important damage*
$9 < SAR < 12$	*Important damage*
$6 < SAR < 9$	*Growing problems*
$5 < SAR < 6$	*Initial problems*
$3 < SAR < 5$	*Low risk*
$1 < SAR < 3$	*No risk*

Ample information on the SAR may be found in the specialist literature.[11]

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3. ADEQUATE LEVELS OF REMINERALIZATION

3.1 Introduction

Remineralisation is understood as being the set of techniques that increase the hardness and alkalinity of water to values producing an index of saturation, also known as the Langelier saturation index (LSI), equal or close to zero and in equilibrium with the atmosphere.

The CO_2 concentration of a water in equilibrium with the CO_2 in the atmosphere naturally defines pH and the combination of carbonates and bicarbonates corresponding to this pH.[1]

In open systems, when the CO_2 content of the water is higher than it should be in equilibrium with the air, the CO_2 escapes to the atmosphere and the pH increases. If, on the contrary, the CO_2 content of the water is lower than it should be in equilibrium with the air, the water will absorb CO_2 from the atmosphere and the pH will decrease.

The objective of remineralisation is, on the one hand, to achieve the point of calco-carbonic equilibrium – that is the point at which pH, calcium and alkalinity do not vary or vary very little in contact with the atmosphere – and, on the other, to accomplish this as accurately as possible in order to minimise the consumption of energy and chemical products, especially CO_2. (See Chapter 4 of this Guide for information on the most important remineralisation techniques).

The process of CO_2 equilibrium with the atmosphere depends on CO_2 partial pressure and temperature.[1] *However, under desalination plant operating conditions only the temperature of the water may vary significantly. In practice these differences are seasonal and do not alter the process of remineralisation in the short term (see Section 3.36 for more details on the impact of temperature on remineralisation).*

This chapter first analyses, based on actual data, the behaviour of different remineralised waters in order to establish their CO_2 concentration in equilibrium with the atmosphere under the conditions existing on the Mediterranean coast. The evolution of pHsat, pHeq and pH (see Chapter 2 of this Guide for definitions of pHsat, pHeq) at different levels of remineralisation is then analysed by means of a mathematical model. The objective is to define the optimum level of remineralisation producing a zero LSI with a water CO_2 content in equilibrium with the atmosphere.

Also verified from the data obtained is the relationship between CO_2 content and the pH of the water. Finally, data are provided on the evolution of the actual pH, bicarbonates and the LSI of the same remineralised waters in contact with the atmosphere, with a view to corroborating the analysis included in the first part of the chapter and to defining optimum levels of remineralisation.

3.2 Materials and methods

In order to analyse the behaviour of remineralised waters in equilibrium with the atmosphere, samples were taken at different desalination plants following remineralisation treatment and "in situ" analyses were performed of pH, EC, temperature, HCO_3^- and CO_3^{2-}.

The samples were subsequently taken to the laboratory where the analyses were repeated and completed with the rest of the parameters. The samples were then left exposed to the atmosphere and softly stirred mechanically, samples being taken for analysis at intervals over a period of some 14 days.

Simulations were carried out using a mathematical model.[4,5]

3.3 Results and discussion

3.3.1 Equilibrium with atmospheric CO_2

The data in Figures 3.1 and 3.2 show that remineralised water tends to reach equilibrium with a CO_2 content of around 0.7± 0.1 mg CO_2/L. It is pointed out that the concentration of CO_2 in the atmosphere is equivalent to approximately 0.56 mg CO_2/L

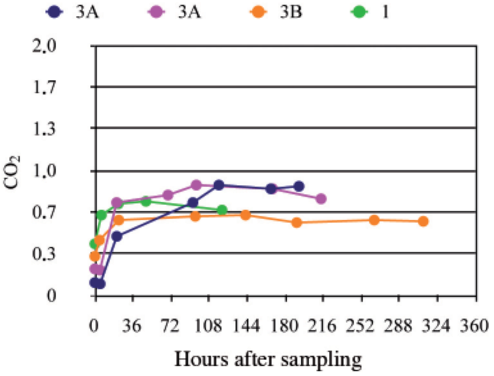

Figure 3.1: Evolution of CO_2 of remineralised water from various desalination plants with infra-dosing of CO_2.

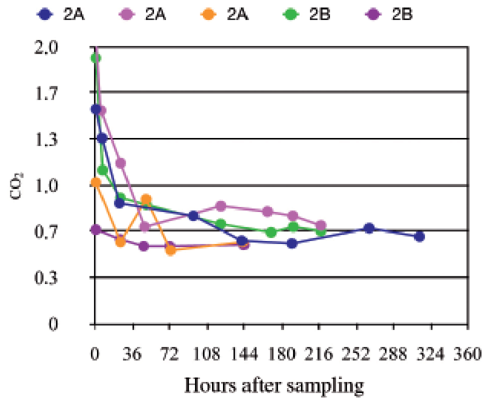

Figure 3.2: Evolution of CO_2 of remineralised water from various desalination plants with slight overdosing of CO_2.

Figure 3.1 shows a series of plants at which the CO_2 content after remineralisation is lower than 0.7 mgCO_2/L. This points out at insufficient dosing of CO_2 and to its being entirely consumed during the process of remineralisation. Consequently, the water tends to adsorb CO_2 from the atmosphere until a state of equilibrium is reached.

In Figure 3.2 the opposite phenomenon occurs. Here the CO_2 content at after remineralisation is higher than in the atmosphere. Consequently, there is a loss of CO_2 from the water, this continuing until equilibrium is reached.

Comparing the data in Figures 3.1 and 3.2 to those shown in Figures 1.5 and 1.6 in Chapter 1, it may be observed that the equilibrium pH of the desalinated water is around 0.3 mg CO_2/L, instead of 0.7 mg CO_2/L as occurs in the case of remineralised water.

3.3.2 Mathematical simulation of remineralisation

In order to better analyse this phenomenon of interaction of desalinated and remineralised water in equilibrium with the atmosphere, two mathematical simulations of the remineralisation process were performed.[4]

Firstly, a desalinated water was used (200 mg TDS/L; pH 6.2; 0.5 mg Ca^{2+}/L; 4,5 mg $CaCO_3$/L;20ºC) and the pH was increased with Na(OH) in order to demonstrate that the lack of calcium is an insuperable factor that prevents a zero LSI from being achieved, however much the pH is increased.

The results are shown in Figure 3.3. As may be appreciated, at a CO_2 concentration of 0.7 mg/L, at which the water would be in equilibrium with the atmosphere, the pH remains at around 7 and the LSI stays between -4 and -3. It is also observed that pHsat and pHeq do not cross even though the pH reaches a value of 9. The crossover occurs at pH =12.

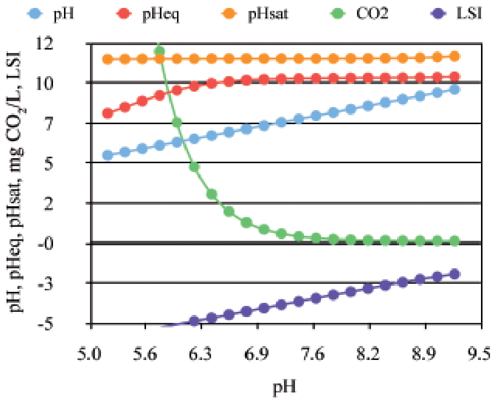

Figure 3.3: Evolution of different values of pH and LSI of desalinated water with the addition of Na(OH).

Secondly remineralised water with 300 mg TDS/L, 22 mg Ca^{2+}/L, 60 mg $CaCO_3$/L of alkalinity, a temperature of 20ºC and a pH of 7 was used, and the pH was increased with Na(OH) in order to check the evolution of pHsat, pHeq and LSI.

Figure 3.4 shows that in this case pHsat, pHeq and pH cross at a value close to 8.2, where the LSI is zero, and that at this value of pH the CO_2 content is around 0.7 mg CO_2/L. Consequently, these would be the conditions under which, in theory, this water would remain stable with the atmosphere, also conserving an LSI equal or very close to zero.

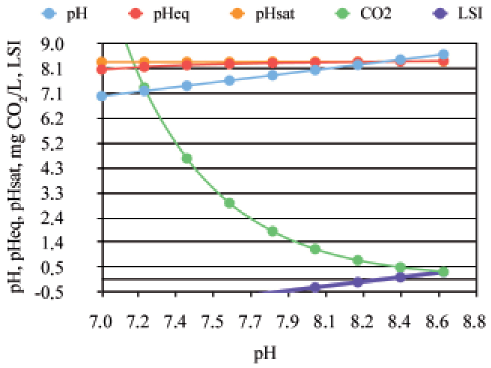

Figure 3.4: Evolution of different values of pH and LSI with the addition of Na(OH) to a water with 20 mg Ca^{2+}, 60 mg $CaCO_3$, 20ºC and starting at pH of 7.

In the next test, different quantities of CO_2 were dosed to a desalinated water, which was left in equilibrium with calcite until pHsat, and consequently zero LSI, was reached. Figure 3.5 shows the evolution of pH, Ca and CO_2 in waters with different degrees of remineralisation and in equilibrium with calcite.

It may be observed that in a situation of equilibrium (LSI equal to zero), the value of 0.7 mg CO_2/L (7 mg/L on the scale in Figure 3.5) corresponds to an alkalinity of 64 mg $CaCO_3$/L, a pH of 8.24 and 24.7 mg Ca^{2+}/L, values that agree with those shown in Figure 3.4, as was to be expected.

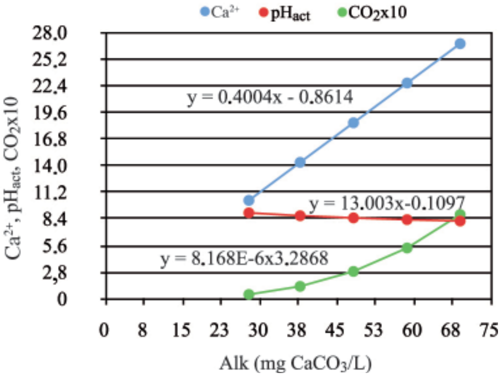

Figure 3.5: Simulation of the composition of waters with different degrees of remineralisation and with LSI = 0.

3.3.3 Obtaining pH in equilibrium with CO_2

Figure 3.6 illustrates the relationship between the pH and CO_2 content of remineralised waters, based on the analised data. As in the case of desalinated waters, a close relationship with the Tillmans[1] formula is confirmed (see Fig 1.1, Chapter 1).

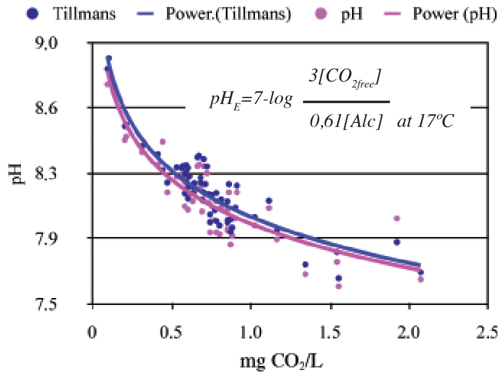

Figure 3.6: Relationship between pH and CO_2 for remineralised waters in accordance with laboratory data and calculation using the Tillmans[1] formula.

On the basis of the regression included in Figure 3.6, obtained for the laboratory data, it can be calculated that for a CO_2 content of 0.7 mg/L, the pH of remineralised water would be around 8.09 (8,13 if using the regression obtained from Tillmans formula). This a value very close to the 8.24 obtained using the theoretical simulation procedure described in the previous paragraph.

3.3.4 Evolution of the pH and LSI of remineralised waters according to field data

Figures 3.7 to 3.12 show the evolution of pH and LSI for remineralised water of different desalination plants, grouped in accordance with the same criteria as applied in Figures 3.1 and 3.2.

The data in Figure 3.7 show that the pH decreases until a state of equilibrium is reached, depending on the degree of CO_2 adsorption in the atmosphere. The decrease in pH is greater the lower the remineralisation, i.e. lower CO_2 dosing (Plant 3A)

Figures 3.9 and 3.10 complement the data in Figure 3.7 for bicarbonates and LSI, respectively.

The data in Figure 3.8 show, on the other hand, that the pH increases when remineralisation is excessive, since the water loses CO_2. The higher the overdosing with CO_2, the more the pH increases after remineralisation.

Figures 3.11 and 3.12 complement the data in Figure 3.8 for bicarbonates and LSI, respectively.

The data in Figure 3.11 also confirm that the equilibrium values of remineralised water are around 73± 4 mg HCO_3/L (60 ± 3 mg $CaCO_3$/L) and the pH around 8.2. These data coincide with those obtained by simulation.

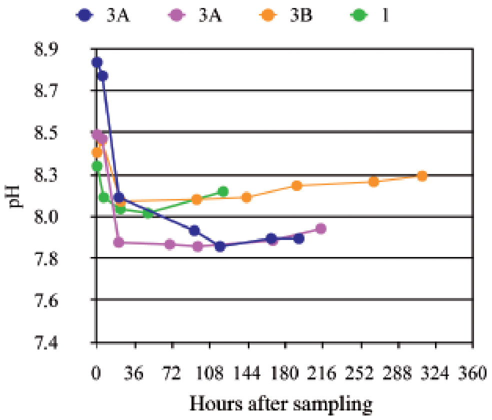

Figure 3.7: Evolution of pH in remineralised water from various desalination plants with infra-dosing of CO_2.

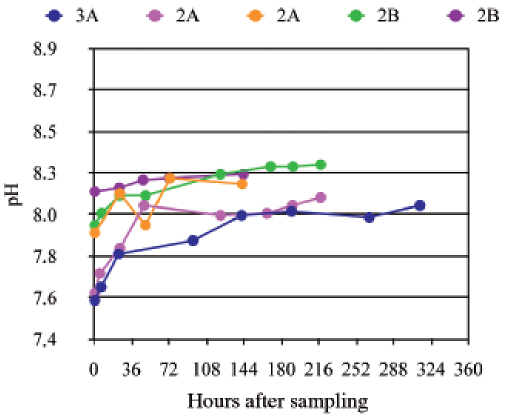

Figure 3.8: Evolution of pH in remineralised water from various desalination plants with slight overdosing of CO_2.

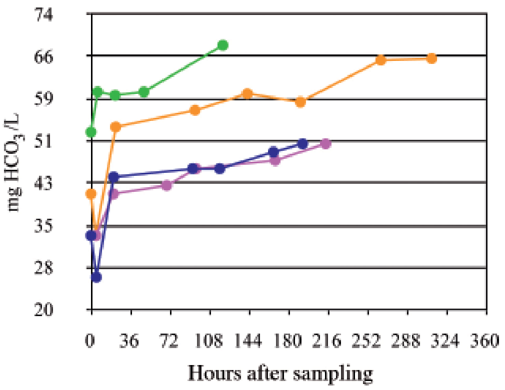

Figure 3.9: Evolution of HCO_3 in remineralised water from various desalination plants with infra-dosing of CO_2.

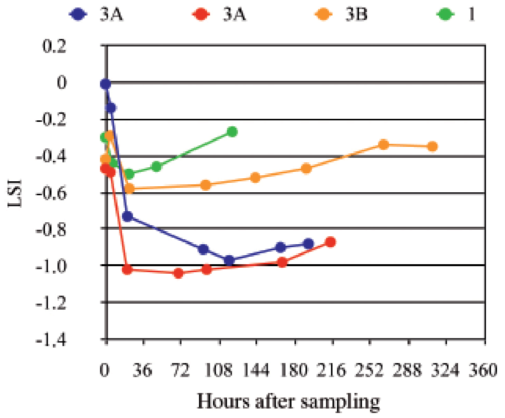

Figure 3.10: Evolution of LSI in remineralised water from various desalination plants with infra-dosing of CO_2.

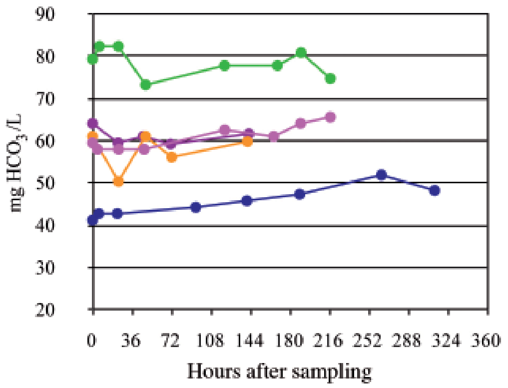

Figure 3.11: Evolution of HCO_3 in remineralised water from various desalination plants with slight overdosing of CO_2.

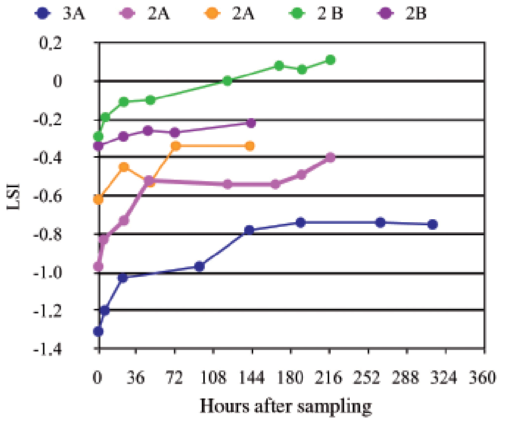

Figure 3.12: Evolution of LSI in remineralised water from various desalination plants with slight overdosing of CO_2.

3.3.5 Relationship between alkalinity and CO_2 dosing

Figure 3.13 illustrates the relationship between the alkalinity of a remineralised water and the required dosage of CO_2, assuming no loss of CO_2 after leaving the reverse osmosis rack and that the efficiency is 100%.

These data have been obtained by mathematical simulation[4] for a water with TDS = 180 mg/L; 1.5 mg Ca^{2+}/L and 20° C. Setting a target pH of 8.2 and a CO_2 content after the remineralisation of 0.7 mg CO_2/L.

As has been seen previously in normal conditions alkalinity of the permeate is usually about 1-2 mg $CaCO_3$/L, so depending on the permeate pH dose of CO_2 can be between 12 and 24 mg CO_2/L.

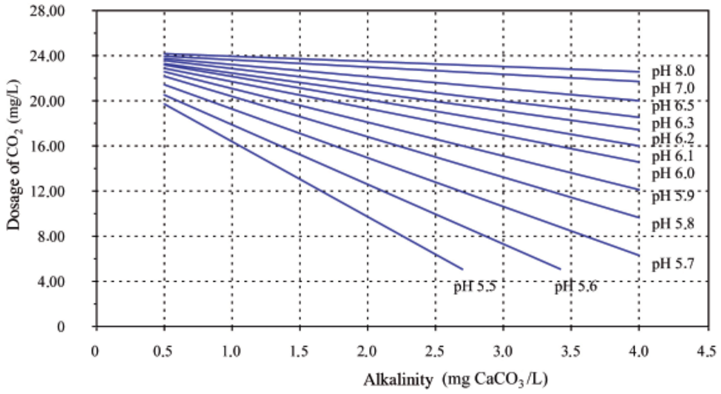

Figure 3.13: Relationship between alkalinity and the dosage of CO_2 to achieve a remineralised water at pH 8.2 and 0.7 mg CO_2/L with a calcite contactor. Simulated data from desalinated water with 180 mg TDS/L, 1.5 mg Ca^{2+}/L and 20ºC.[4]

3.3.6 Effect of temperature on LSI

Figure 3.14 illustrates the relationship between the alkalinity of a water with different levels of remineralisation and LSI, at different temperatures and for an open system, i.e. in equilibrium with the atmosphere. The data have been obtained by mathematical simulation[4] and refer to a remineralisation with CO_2 and calcite contactor.

There is a direct relationship between increased alkalinity and increased LSI. As the alkalinity is obtained by adding more CO_2, this implies an excess of CO_2 after remineralisation. This excess CO_2 is lost after treatment as the water reaches equilibrium with the atmosphere. Thus, the LSI becomes positive. At the same time an increase in temperature further increases this effect, since the dissolved CO_2 decreases with increasing temperature. The effect of temperature changes on LSI in the operating ranges of desalination plants is around ±0.1 LSI.

In Figure 3.14 it may be seen that a water remineralised to 100 mg $CaCO_3$/L of alkalinity at a temperature of 40ºC does not exceed an LSI value of 0.7 once in equilibrium with the atmosphere. At this level of remineralisation corresponds a calcium content of 40 mg Ca^{2+}/L.

This data underline, and as has been indicated by other authors[2,3], that remineralised water do not precipitate readily at LSI values of 0.7 and temperature 40°C provided that pH does not exceed the value of 8.4 after of remineralisation. This is relatively easy to achieve with $CaCO_3$ contactor. While not so with with $Ca(OH)_2$ treatment. (See Section 5.3 of this Guide).

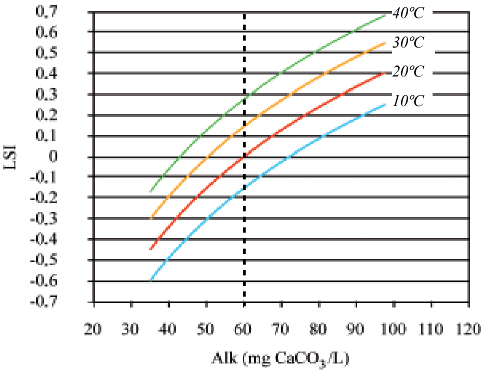

Figure 3.14: Relationship between LSI and alkalinity for remineralised waters at different temperatures. Simulated data.[4]

3.4 Conclusions

3.4.1 Adequate levels of remineralization

According to this study, it is considered that remineralised water should present the conditions shown in Table 3.1 for a range of temperatures of between 14ºC and 25ºC.

TABLE 3.1: *CHARACTERISTICS RECOMMENDED FOR DESALINATED WATERS WITH AN OPTIMUM LEVEL OF REMINERALISATION.*

Parameter	*Range*
pH	*8.2 ± 0.1*
Alk (mg $CaCO_3$/L)	*56 ± 3*
HCO_3^- (mg/L)	*68 ± 3*
Ca^{2+} (mg/L	*21 ± 2*
CO_2 (mg/L)	*0.7 ± 0.1*
LSI	*± 0.15*

There is the option of adding more CO_2 to increase the alkalinity and hardness but then the remainder will have excessive CO_2 to be in equilibrium with the atmosphere and most of it will be lost in a few hours driving up the pH and thereby obtaining a positive LSI.

The effect of temperature changes on LSI in the operating ranges of desalination plants is around ±0.1 LSI.

In many water networks LSI values between +0.1 to +0.5 are requested to protect the installations. This is achieved in the case of $CaCO_3$ postreatment by slightly increasing the pH by adding NaOH (2-4 mg NaOH/L). In the $Ca(OH)_2$ installations this is done with a slight overdose of $Ca(OH)_2$. In some occasions, technical limitations in controlling the exact dose of $Ca(OH)_2$ may cause an increase in turbidity above 1 NTU.

3.5 References

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4. INDIRECT CALCULATION OF THE LSI AND SAR OF REMINERALISED WATER FROM DATA ON EC AND PH PRIOR TO AND FOLLOWING REMINERALISATION

4.1 Introduction

As indicated in Chapter 2, the LSI is calculated from the values of EC_{25} or TDS, Ca^{2+}, Alk, pH and temperature.

In practice, EC_{25}, pH and temperature are normally measured continuously in the majority of desalination plants. This is not the case for calcium, which requires a specific and more costly probe.

For its part, alkalinity cannot be analysed continuously since there are no commercial systems making this possible.

At certain desalination plants measuring devices have been installed for total inorganic carbon, which may be correlated with alkalinity; however, the equipment in question is costly, as a result of which its implementation is limited.

Consequently, there is a need for a simple method making it possible to estimate with some accuracy the increase in alkalinity and hardness achieved through remineralisation.

In the case of traditional remineralisation, as set out in this Guide, the reactions involved are as follows:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad [1]$$

$$Ca(OH)_2 + 2\,CO_2 \overset{H_2O}{\rightleftharpoons} Ca^{2+} + 2HCO_3^- \qquad [2]$$

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

In processes in which hydrochloric or sulphuric acid is added instead of CO_2, the proportions are different; however, these cases are not considered in the present Guide.

Consequently, and in view of the above, investigation of the relationship between the increases of $\Delta EC_{25}=EC_{25(r)} - EC_{25(o)}$ and $\Delta Alk=Alk_{(r)} - Alk_{(o)}$ is justified, in order to be able to extrapolate the alkalinity values of remineralised water.

This work has been carried out on the basis of actual data taken at different desalination plants and of theoretical calculations based on the contribution of each ion to the conductivity of the water, as published in Standard Methods.[1]

4.2 Materials and methods

First the data from the laboratory analysis have been used to estimate the value of the ratio $\Delta EC_{25}/\Delta Alk$.

Furthermore, the value of the quotient has been obtained by first using a model of remineralisation with calcite[2] *with different levels of CO_2 dosing and by calculating the EC_{25} of the remineralised water using the ion contribution method published in Standard Methods.*[1]

4.3 Results

Figure 4.1 shows the results of the calculations of $\Delta CE_{25}/\Delta Alk$, obtained from real data of three desalination plants, and by calculating the ionic contribution to the EC for three typical remineralised waters with increasing levels of EC.

To simulate the remineralised water quality it has been considered that the water reaches a zero LSI from a permeate with a pH of 6.2 and where the values of Na, K and Cl vary proportionally according to the EC following the relations in Figure 1.2. The values of Mg^{2+}, Ca^{2+} and SO_4^{2-} were estimated as $Mg^{2+} = 1.8 \times K^+$; $Ca^{2+} = Mg^{2+}/1.7$; $SO_4^{2-} = 0.9 \times K^+$.

Table 4.1 illustrates the initial composition of these desalinated waters. From there, dose of 20, 27 and 35 mg CO_2/L was applied and the composition of the remineralised water was calculated using a simulation model[2]*. The theoretical value of the EC remineralised water was calculated according to the criteria of SM-20101.*

The theoretical results presented in Figure 4.1 for the three levels of EC: 300, 500 and 700 µS/cm, point to a clear reduction ratio $\Delta CE_{25}/\Delta Alk$ with increased conductivity. As can be seen also on Figure 4.1, this effect is applicable, although fairly diffuse, with the data obtained from various desalination plants.

With the aim of analysing the impact posed by the EC on the $\Delta CE_{25}/\Delta Alk$ ratio, the theoretical study has been extended to obtain the relationship between the EC of the permeate and the coefficient value. Figure 4.2 illustrates this relationship. For Figure 4.2 only the dosage of 27 mg CO_2/L has been used, which corresponds to an equilibrium pH of 8.14.

Note: EC_{25}: EC refered to 25º

TABLE 4.1: *THEORETICAL COMPOSITION OF DESALINATED WATER IN PROPORTION TO DECREASING CE_{25}. VALUES OBTAINED USING CRITERIA EXPLAINED IN THE TEXT.*

CE_{25} µS/cm	700	600	500	400	300	200	100
pH	6.2	6.2	6.2	6.2	6.2	6.2	6.2
Ca^{2+}, mg/L	1.67	1.44	1.22	0.99	0.77	0.54	0.31
Mg^{2+}, mg/L	2.87	2.49	2.10	1.71	1.32	0.93	0.54
Na^{+}, mg/L	108.64	93.15	77.66	62.17	46.68	31.19	15.70
K^{+}, mg/L	5.17	4.47	3.77	3.07	2.37	1.67	0.97
Cl^{-}, mg/L	205.31	175.28	145.25	115.22	85.19	55.16	25.13
SO_4^{2-}, mg/L	4.71	4.07	3.43	2.80	2.16	1.52	0.89
HCO_3^{-}, mg/L	2.17	1.88	1.58	1.29	1.00	0.70	0.41

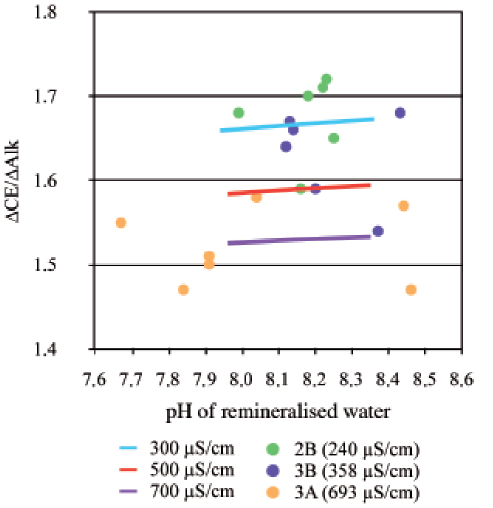

Figure 4.1: Relationship between the pH of remineralised water and the quotient $\Delta EC_{25}/\Delta Alk$. Lines for 300, 500 and 700 µS/cm have been obtained by mathematical simulation.[1,2]

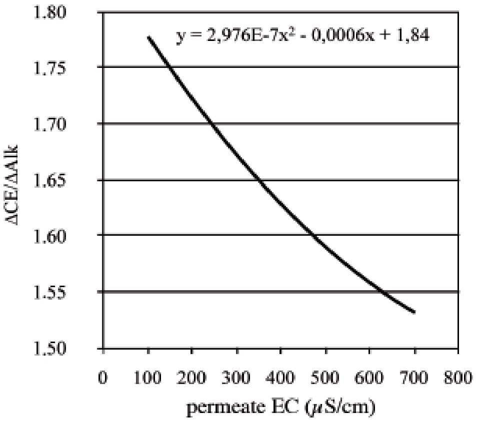

Figure 4.2: Relationship between permeate EC and the quotient $\Delta CE_{25}/\Delta Alk$ for waters remineralised up to pH 8.2. The line has been defined using a mathematical simulation of remineralisation.[1,2]

TABLE 4.2: *COMPARATIVE STUDY OF LSI CALCULATION BY THE CALCULATION METHOD USING $\Delta EC_{25}/\Delta ALK=1.8$ AND BY ACTUAL LABORATORY ANALYSES.*

Plant No. (date)	3A (1-06-09)		3A (11-06-09)		3B (11-06-09)		2B (03-06-09)		2B (23-06-09)		6 (27-05-09)		6 (19-05-09)	
	Calc.	Lab	Calc.	Lab	Calc.	Lab	Calc.	Lab	Calc.	Lab	Calc.	Lab	Calc.	Lab
$CE_{25(r)}$, µS/cm	777.3	777.3	729.7	730.0	416.4	416.4	325.6	325.6	341.9	341.9	694.0	694.0	687.9	687.9
$CE_{25(O)}$, µS/cm	728.3	728.3	656.9	660.0	358.1	358.1	220.4	220.4	259.6	259.6	639.0	639.0	610.8	610.8
ΔCE_{25}, µS/cm	49.0	49.0	72.8	70.0	58.3	58.3	105.2	105.2	82.3	82.3	55.0	55.0	77.1	77.1
$Alk_{(r)}$, mg $CaCO_3$/L	33.00	35.00	47.85	33.75	35.95	38.75	61.78	67.50	48.99	52.50	36.35	40.00	50.16	47.50
$Alk_{(o)}$*, mg $CaCO_3$/L	1.61	1.61	1.61	1.61	0.90	0.90	0.70	0.70	0.70	0.70	1.50	1.50	1.50	1.50
ΔAlk	31.39	31.94	46.24	31.89	35.05	37.85	61.08	64.30	48.29	51.80	34.85	58.04	48.66	46.00
$\Delta CE_{25}/\Delta Alk$	1.56	1.53	1.57	2.20	1.66	1.54	1.72	1.64	1.70	1.59	1.58	0.95	1.58	1.68
pH	8.46	8.46	7.60	7.60	8.37	8.37	7.99	7.99	8.16	8.16	7.83	7.83	9.04	9.04
Ca^{2+}	13.20	12.64	19.14	13.58	14.38	15.80	24.71	28.23	19.60	21.42	14.54	15.17	20.06	17.22
Temperature, ºC	23.70	23.70	23.20	23.20	22.10	22.10	22.10	22.10	22.50	22.50	20.40	20.40	19.80	19.80
LSI-2330	-0.31	-0.31	-0.83	-1.14	-0.29	-0.22	-0.18	-0.09	-0.21	-0.14	-0.89	-0.83	0.54	0.45

**) The value of $Alk_{(o)}$ has been estimated from the EC since the method used in the laboratory does not permit a precise determination of alkalinity values < 5 mg $CaCO_3$/L.*

4.3.1 Indirect calculation of LSI from the quotient $\Delta EC_{25}/\Delta Alk$

According to Figure 4.2:

$\Delta CE/\Delta Alk = 2{,}976E\text{-}7 \times [CE_{25(o)}]^2 - 0{,}0006 \times CE_{25(o)} + 1{,}84$ [3]

Following, calcium of the remineralised water has been estimated as $Ca^{2+}_{(r)} = Alk_{(r)}/2{,}5$.

For its part the pH used has been that measured "in situ", along with that corresponding to temperature.

The results are shown in Table 4.1 and the relationship between the calculated and actual LSI values is included in Figure 4.3

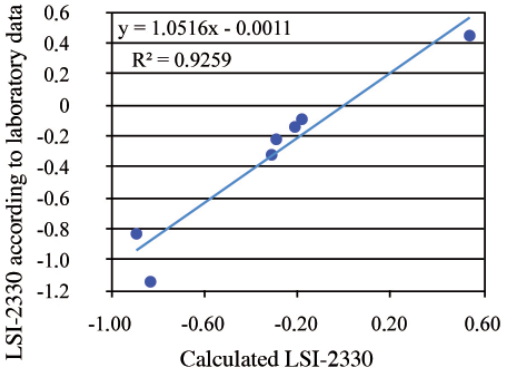

Figure 4.3: Relationship between LSI calculated in accordance with the criteria of paragraph 4.3.1 and the laboratory data.

4.3.2 Indirect calculation of SAR

The correlation established for desalinated water should be used for the calculation of the SAR (see Figure 1.2 in Chapter 1).

$Na_{(r)}(mg/L) = Na_{(0)}(mg/L) = 0.1549 \times EC_{25(0)} + 0.2137$

The following may be assumed in the case of magnesium:

$Mg_{(r)}{}^{2+} = Mg_{(0)}{}^{2+} = 1.8 \times mg\ K^+/L$

or

$Mg_{(r)}{}^{2+} = Mg_{(0)}{}^{2+} = 2.5\ mg\ Mg^{2+}/L$.

The value of Ca^{2+} *in mg/L is obtained from the relation:*

$Ca^{2+}_{(r)} = Alk_{(r)}/2.5$

4.3.3 Sampling and analytical considerations

As has been observed in previous chapters, it is importar ≈ 1.6 *in sampling to prevent the loss of* CO_2. *Consequently, it is advisable to optimise the sampling by avoiding aeration. The samples of pH and temperature, in particular, should preferably be taken in line. Otherwise it is recommended that the protocol specified in Chapter 5 of this Guide and specific references*[2,4] *be adhered to.*

It is also advisable to reference the EC measures to 25ºC. Finally, the alkalinity values should be obtained out following laboratory procedure SM-2320B.[5]

4.4 Conclusions

The results obtained indicate that the LSI of remineralised water ($LSI_{(r)}$) *may be calculated from the increase in* EC_{25} *produced by remineralisation, using the quotient:*

$\Delta EC_{25}/\Delta Alk \approx 1{,}65$ *(or use the relationship of Fig. 4.2)*

Where:

$\Delta Alk = Alk_{(r)} - Alk_{(o)}$
$\Delta EC_{25} = EC_{25(r)} - EC_{25(o)}$

$Alk_{(o)}$ *varies from 0.5 and 2.8 mg* $CaCO_3/L$ *for values of* $EC_{25(0)}$ *between 250 µS/cm and 700 µS/cm respectively.*

The value of $Ca_{(r)}$ *of remineralised water may be calculated on the basis of the ratio* $Ca_{(r)} = Alk_{(r)}/2.5$.

The values of $pH_{(r)}$ *and* $T_{(r)}$ *will be those acquired "in situ" from the measuring equipment installed in line.*

Once all the parameters have been obtained, the method used to calculate $LSI_{(r)}$ *should be SM2330.*[3]

This procedure allows $LSI_{(r)}$ *to be estimated within ±0.05 in the range of operation of desalination plants (LSI ± 0.5). In accordance with the study performed, and in order to achieve the optimum levels referred to in Table 4.1, the increase in alkalinity should be at least 55 mg* $CaCO_3/L$.

This implies that the increase in EC_{25} *caused by remineralisation should be at least:*

$\Delta CE_{25} = 85 - 97\ \mu S/cm$

For the calculation of $SAR_{(r)}$, *the following may be assumed:*

$Ca_{(r)} = Alk_{(r)}/2.5$
$Mg_{(r)} = 2.5$ *mg/L and*
$Na_{(r)}(mg/L) = 0.1549 \times EC_{25(0)} + 0.2137$.

The sampling conditions should be optimised in order to prevent the loss of CO_2 *and to obtain pH and temperature* *values as close as possible to the operating conditions prior and after the remineralisation system.*

4.5 References

1. *WATER-PRO Schott Software, Published by ChemSW®, Inc.; http://www.chemsw.com.*
2. *STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER. Method 2510: Conductivity. 21st ed. 2005. ISBN 0-87553-047-8.*
3. *STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER. Method 2330: Calcium Carbonate Saturation. 21st ed. 2005. ISBN 0-87553-047-8.*
4. *STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER. Method 4500-H^+, pH Value. 21st ed. 2005. ISBN 0-87553-047-8.*
5. *STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER. Method 2320B, Alkalinity, Titration Method. 21st ed. 2005. ISBN 0-87553-047-8.*

5. TECHNIQUES FOR THE REMINERALISATION OF DESALINATED WATERS

5.1 Introduction

The objective of remineralisation techniques is to increase the calcium content and alkalinity of desalinated water to values allowing an LSI close to zero (LSI ± 0.5 range of spanish RD 140/2003) to be attained. In certain cases, as generally occurs with desalinated waters destined for supply, the objective is also to achieve a remineralised water that is stable in contact with the atmosphere.

Remineralisation reduces the aggressive nature of desalinated water by increasing LSI and bicarbonate content with respect to chlorine and sulphates.

In the case of waters for agricultural use, remineralisation also improves water quality as in increases the proportion of calcium with respecto to sodium.

Figure 5.1 illustrates the principle of remineralisation of desalinated waters, from the point of view of CO_2 *<=>* HCO_3^- *<=>* $CO_3^=$ *equilibrium for a normal desalinated water: 200 mg TDS; pH = 6.0; 4 mg* HCO_3*/L; 3 mg* CO_2*/L; 1.5 mg* Ca^{2+}*/L and T=20 ºC.*

As the diagram illustrates, the remineralisation process increases bicarbonate content to 75 mg/L, consuming the CO_2 *until it is left at a value of 0.7 mg/L; in other words, in equilibrium with the atmosphere. This increase in bicarbonates is accompanied by an increase in pH, in the case in hand to a pH of 8.2.*

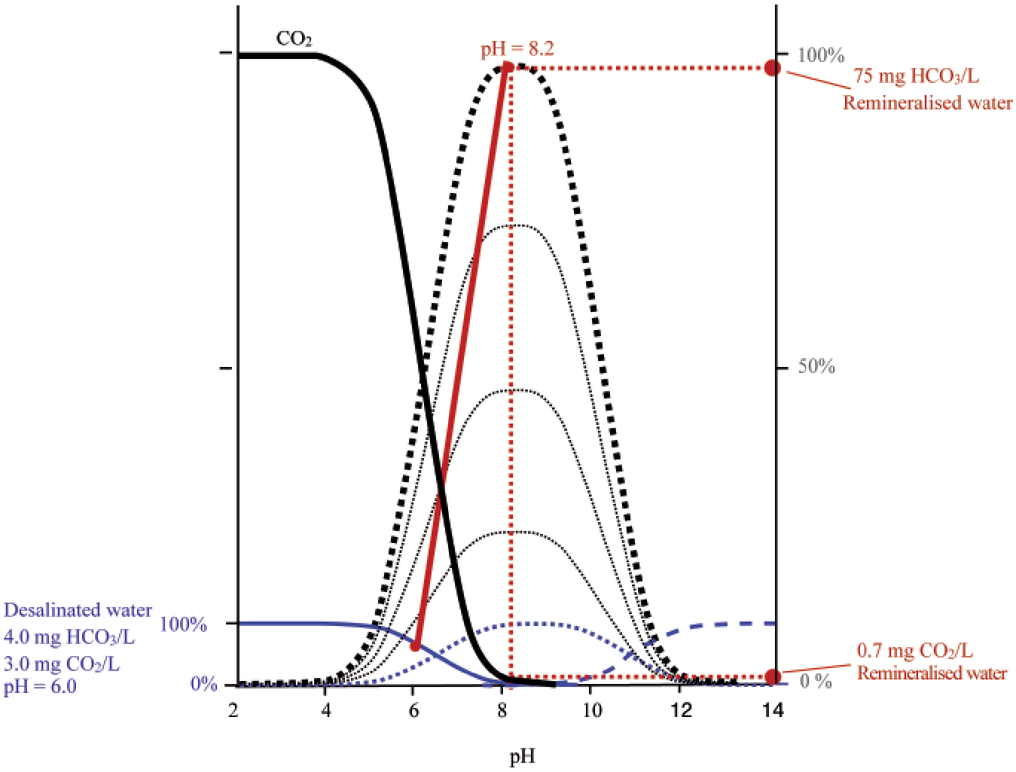

Figure 5.1: Aspects of CO_2-HCO_3 equilibrium in the process of remineralisation of desalinated water

TABLE 5.1: *TECHNIQUES FOR THE REMINERALISATION 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/m³ of alkalinity
1	Calcium carbonate + Carbon dioxide	$CaCO_3 + CO_2 + H_2O \fallingdotseq Ca^{2+} + 2(HCO_3^-)$	50.1 mg $CaCO_3$ 100% 22 mg CO_2	20 mg Ca^{2+}
2	Calcium hydroxide + Carbon dioxide	$Ca(OH)_2 + 2CO_2 \fallingdotseq Ca^{2+} + 2(HCO_3^-)$	37.1 mg $Ca(OH)_2$ 100% 44 mg CO_2/L	20 mg Ca^{2+}
3	Dolomite + Carbon dioxide	$MgOCaCO_3 + 3CO_2 + 2H_2O \fallingdotseq Mg^{2+}\ Ca^{2+} + 4(HCO_3^-)$	35.1 mg $MgOCaCO_3$ 100% 33 mg CO_2	6,1 mg Mg^{2+} 10 mg Ca^{2+}
4	Calcium carbonate + Sulphuric acid	$2CaCO_3 + H_2SO_4 \fallingdotseq Ca^{2+} + 2(HCO_3^-) + Ca(SO_4)$	100.1 mg $CaCO_3$ 100% 49 mg H_2SO_4 100 %	40,1 mg Ca^{2+} 48 mg SO_4^{2-}
5	Calcium chloride + Sodium bicarbonate	$CaCl_2 + 2NaHCO_3 \fallingdotseq Ca^{2+} + 2(HCO_3^-) + 2NaCl$	55.5 mg $CaCl_2$ (100%) 84 mg $NaHCO_3$ (100%)	23 mg Na^+ 20 mg Ca^{2+} 35,5 mg Cl^-

Table 5.1 illustrates the different remineralisation techniques.

Although five remineralisation techniques are shown in Table 5.1, the most widely used in practice are techniques 1 and 2.

Summarised below is some specific information on these two techniques. Further information may be found in the literature.[1 to 17]

5.2 Remineralisation with $CaCO_3 + CO_2$

This type of treatment uses calcium carbonate to neutralise aggressive carbonic gas during filtration, giving rise to calcium and bicarbonate in solution and thus increasing the alkalinity and hardness of the water. The reaction is as follows:

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2(HCO_3^-) \qquad [1]$$

The filtering material normally used is calcite of a purity of around 99%, normally with a granulometry of around 1-4.3 mm, although 1-3 mm is preferred.

The filtration beds are installed in filters that are either open or closed under pressure. Both filtering directions are possible: upflow or downflow. There is a variation on the upflow filtration beds, known as continuous feed or constant height beds.[17] *(See also Figures 5.12, 5.13 and 5.15).*

In the case of downward flow, the neutralising material also acts as the mechanical filter, and as such is prone to becoming clogged, depending on the percentage of fines in the calcite. This generally makes it necessary to perform backwashing operations every 10-14 days. This backwashing is normally carried out coinciding with the recharging of the filters. The backwashing is performed in the following sequence:

1. *Air: 3 min at 80 Nm³/h and m²*
2. *Air: 5 min at 80Nm³/h and m² + water: at 20 m/h.*
3. *Water: 5 min at 30 m/h*
4. *Water: 5 min at 50 m/h.*
5. *Water: 30 min at rated flow (10-16 m/h).*

The annual consumption of water in these backwashing operations is equivalent to the production of the plant of one day. When filtering is performed from the bottom upwards, the procedure is made to coincide with the charging process, although step 4: Water 5 min at 50 m/h is not necessary.

In the case of upflow and constant height beds, the only maintenance required is periodic sponging or expansion once or twice a year. The objective of sponging is to eliminate the preferential paths that might have been generated in the bed. The following sequence is recommended for sponging:

1. *3 min with air at 80 Nm³/h and m²*
2. *30-45 min with water at rated flow (10-16 m/h)*

It is recommended in all cases that there be an initial flushing of the beds in order to obtain a turbidity of less than 1 NTU. There are procedures for the filling and cleaning of the beds.[18] *A variation used in practice for larger beds is as follows:*

1. *3 min with air 80 Nm³/h and m²*
2. *10 min at 32 m/h*

This sequence is repeated 4 or 5 times depending on the height of the bed and the percentage of fines in the calcite. It is important to point out that the cleaning of the beds, especially after the initial charging, should be performed in accordance with these recommendations, since in the case of insufficient backwashing operations a sufficient amount of material remains in the bed to cause problems of turbidity for some time.

It is recommended that the height of the filtering layer be between 1.5 and 3 m. Highest beds present problems with cleaning operations. Filtering velocity of between 10 and 16 m/h are commonly used.

The main design criteria for normal upflow calcite beds and constantly fed upflow calcite beds are described in detail below.

5.2.1 Rate of upflow

In constantly fed upflow calcite beds (Fig. 5.1.4), the rate of ascent determines the turbidity of the water at the outlet. Figure 5.2 illustrates this relationship for beds with particles of 1-3 mm. The tests were performed after the plant had been in operation for several months. These data were subsequently corroborated with other plants.

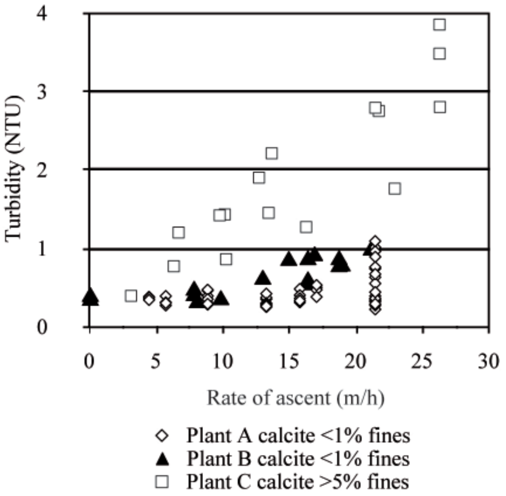

Figure 5.2: Relationship between the rate of ascent and turbidity of outlet water for calcites with different percentages of fines.

The data show that the value of 1 NTU is generally exceeded as from 20 m/h. In practice speeds of between 10 and 16 m/h are selected. In practice, calcite contactors with without constant feeding system velocities are also operated at these velocities.

5.2.2 Empty bed contact time

Calculation of the Empty Bed Contact Time (EBCT) is performed by means of a mathematical simulation of the process of calcite bed saturation.[14] This simulation has been contrasted with a large volume of field data. It is assumed that the calcite will have a purity of 99% and a granulometry of 1-3 mm. The simulation results shown in Figures 5.3 to 5.7 refer to a normal permeate: pH = 6.2; 4 mg HCO_3/L; 1.5 mg Ca^{2+}/L; 3 mg CO_2/L; 200 mg TDS/L and T = 22ºC., and to a dosing of 23 mg CO_2/L.

According to these graphs, a contact time of 11 minutes is normally selected. For colder waters and below 14ºC, 14 - 20 minutes are used. (see Figures 5.8 and 5.9).

When the aim is to increase alkalinity and hardness by increasing the dose of CO_2, for example to 70 mg CO_2/L, an EBCT of 18-20 minutes is required to reach the almost flat phase of the saturation curve.

In practice the height of the calcite beds ranges from 1 to 3.5 metres, and is frequently around 2 m.

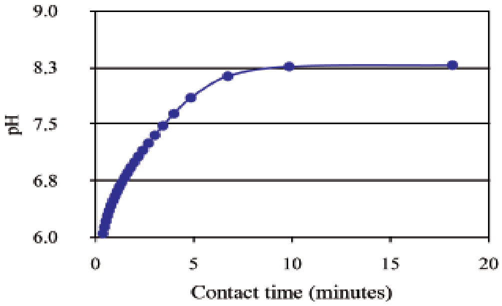

Figure 5.3: Relationship between pH and contact time in minutes for an upflow calcite bed *(see text for details on the simulation)*

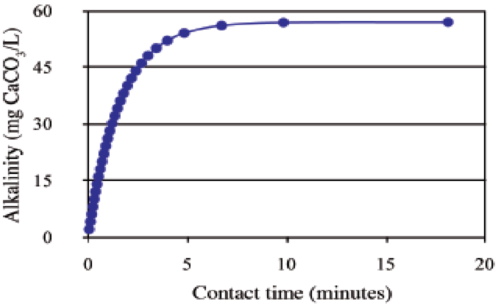

Figure 5.4: Relationship between alkalinity and contact time in minutes for an upflow calcite bed *(see text for details on the simulation)*

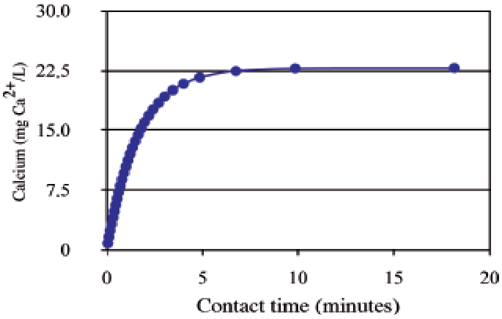

Figure 5.5: Relationship between calcium concentration and contact time in minutes for an upflow calcite bed *(see text for details on the simulation)*

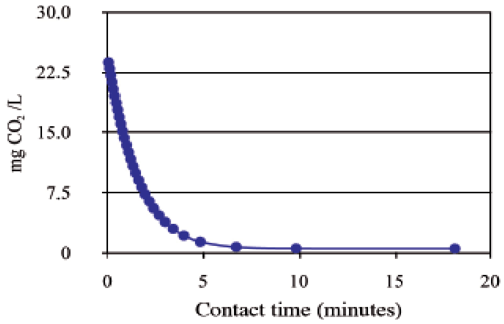

Figure 5.6: Evolution of CO_2 consumption and contact time in minutes for an upflow calcite bed *(see text for details on the simulation)*

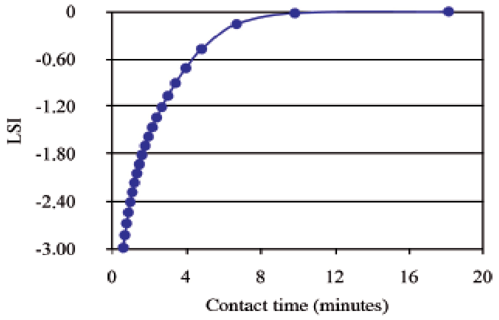

Figure 5.7: Evolution of LSI and contact time in minutes for an upflow calcite bed *(see text for details on the simulation)*

5.2.3 Effect of temperature

In certain cases it is advisable to adjust the contact time to more extreme temperature conditions. The drop in temperature causes the speed of reaction to decrease, this in turn causing a drop in the performance of the calcite beds. Figure 5.8 shows this drop for a calcite bed with an EBCT of 12.3 min and a rate of ascent of 12.8 m/h. The data show that the cooling of the bed prevented adequate remineralisation and the pH of 8.2 from being attained.

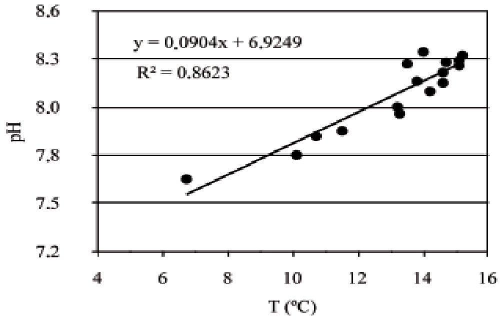

Figure 5.8: Relationship between pH and water temperature for a calcite bed with a contact time of 12.3 minutes and a rate of ascent of 12.8 m/h.

Figure 5.9 illustrates the relationship between temperature and contact time to reach a pH of 8.2 in desalinated waters. This curve has been contrasted with data from the literature and practical experience from this author.[19]

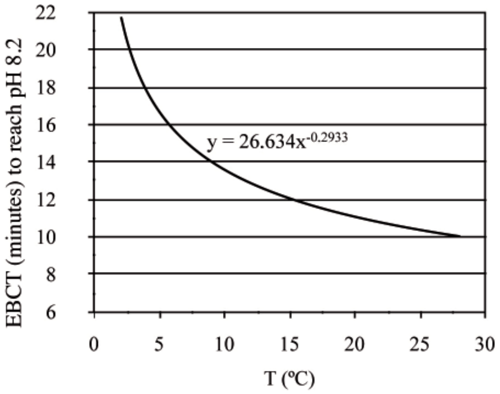

Figure 5.9: Relationship between EBCT and temperature for upflow calcite beds *(± 5%).*

5.2.4. Head loss of calcite bed and fluidisation

Fluidisation of the bed is sometimes necessary for the removal of fines. Figure 5.10 shows the relationship between loss of head and rate of ascent for a bed with particles measuring 1-3 mm in diameter. According to these data, expansion of the bed begins at 30 m/h and complete fluidisation is achieved as from 50 m/h.

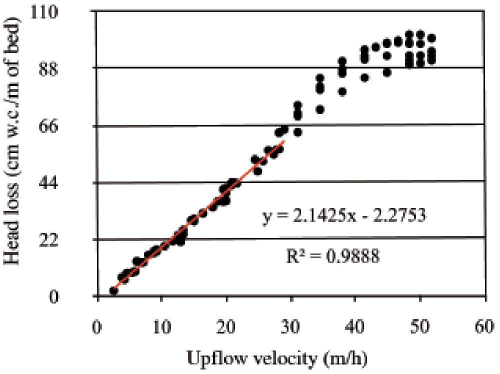

Figure 5.10: Relationship between head loss and upflow velocity for calcite beds. Particles measuring 1-3 mm in diameter

In order to obtain a water with a turbidity of less than 1 NTU after backwashing, the upflow velocity of (10-15 m/h) should be maintained for some 30-45 minutes. This is the same time as is required to return to normality when the flow of water is suddenly increased as a result of the entry into operation of a new reverse osmosis rack. Figure 5.11 illustrates this evolution.

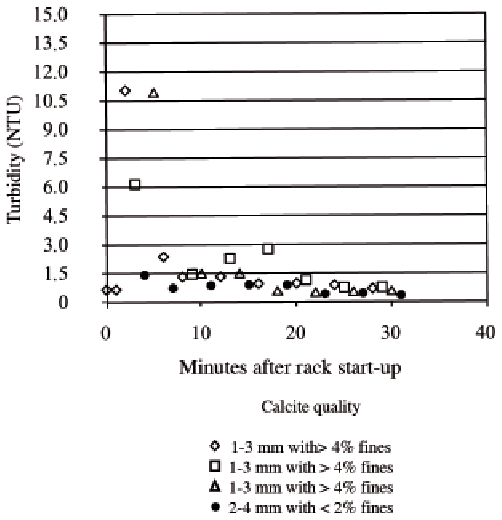

Figure 5.11: Relationship between turbidity and time following rack start-up.

5.2.5. Calcite quality

It is important that the calcite be free from dust (Ø < 40 µm) and have a uniform particle size. This should be 1-3 mm, although plants are frequently found operated with particle size of 2-4 mm.

The quality recommended for correct operation of both upward and downward flow beds is summarised in Table 5.2. It must also have the certificate for use in drinking water supply.

***TABLE 5.2:** RECOMMENDED CALCITE QUALITY. VALUES IN % DRY WEIGHT.*

Parameter	*Recommended value*
Purity	*> 97%*
SiO_2	*< 1%*
Al_2O_3	*< 1%*
MgO	*< 0.3%*
SO_3	*< 1%*
Fe_2O_3	*< 0.1%*
Specific weight (t/m^3)	*2.7*
SW dry granulate (t/m^3)	*1.5*
SW moist granulate (t/m^3)	*1.8*
% particles smaller than 0,3 mm	*< 3%*
% particles smaller than 0,1 mm	*< 1%*
Insoluble material >50 µm	*< 0.5%*

5.2.6 Final Na(OH) dosing to achieve positive LSI

In certain cases it is necessary to add Na(OH) in order to increase the pH of the water and achieve a positive LSI. The dose in these cases is generally 2 ± 0,5 mg Na(OH)/L at 33% purity.

5.2.7 Design of calcite beds

Calcite beds are designed in the form of rectangular cells of different sizes or circular tanks. In the case of beds without continuous dosing, the maximum flow per cell may reach 20,000 m^3/d.

Figure 5.12 shows the external appearance of a traditional downward flow cell. In the case of upflow beds of constant height (i.e with constant feeding), the treatment capacity of the rectangular cells does not generally exceed 8,000 m^3/d, this value amounting to 2,500 m^3/d in the case of circular tanks (3 m in diameter).

Figures 5.13 and 5.14 show an example of the design of constant height calcite beds.[19]

Figure 5.15 shows the charging area of the calcite silos of an upflow constant height plant.

Figure 5.12: View of the cells of a downward flow calcite plant.

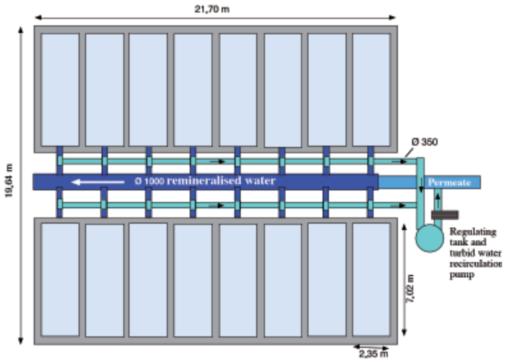

Figure 5.13: Plant showing the intake of remineralised water and the turbid water re-injection circuit.

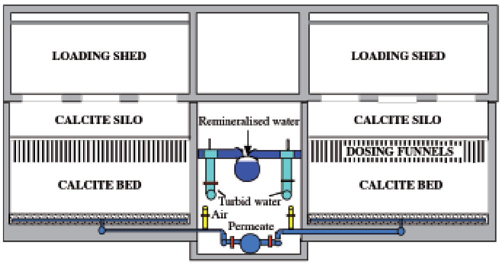

Figure 5.14: Cross-section of upflow constant height calcite cells showing the feed and collection of turbid and remineralised waters

Figure 5.15: View of calcite silo charging area of an upflow constant height calcite plant

5.2.8 CO_2 dosing

Generally a certain dose of CO_2 to desalinated water is required to perform an adequate remineralisation. As indicated in Section 3.3.5 of Chapter 3 of this Guide, the dosage of CO_2 to reach the goal of remineralisation proposed in Table 3.1 varies with alkalinity (i.e. bicarbonate) of desalinated water. As shown in Figure 3.13 for water with an alkalinity of 1.5 mg $CaCO_3$ a dosage of about 18 mg CO_2/L is required.

The dosage of CO_2 works well with direct injection pipe in down flow. The water velocity in the pipe before and after injection point should be maintained at 0.07 ± 0.02 m/s to avoid the drag of the bubbles. The pressure differential between water and gas should be around 0.25 bars. Increased differential pressure increases the size of the bubbles. The contact time between the injection and the entrance to the beds of calcite can be reduced to about 5 seconds if the above conditions are met.

Not recommended is the dosage of CO_2 in horizontal pipe since the bubbles tend to rise quickly to the upper wall and dragged with the flow water. The placement of a horizontal mixer involves a certain head loss and no experimental data have been found to justify this solution. The dosage of the part of flow at higher pressure (2-6 bar) is expensive as it demands energy and it is rare in desalination plants.

5.3 Remineralisation with $Ca(OH)_2$ + CO_2

Hardness and alkalinity make-up in desalinated water is accomplished in keeping with the following reaction:

$$Ca(OH)_2 + 2CO_2 \overset{H_2O}{\leftrightharpoons} Ca^{2+} + 2(HCO_3) \qquad [2]$$

As is shown in Figure 5.16, the response of the desalinated water to dosing with $Ca(OH)_2$ is practically immediate.

However, with an increase in the CO_2 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 $CaCO_3$/L. In any case, the process is difficult to control.

Figure 5.17 shows the components of a typical lime slurry and CO_2 dosing installation. As may be appreciated, the CO_2 is injected directly before the lime slurry into the product water tank. The contact time in the tank is sufficient to guarantee a complete reaction.

In some plants the dosage of CO_2 is made after the dosing of lime slurry.

In other cases the dosing is accomplished directly in the piping. Also, a by-pass is sometimes used for mixing of the slurry prior to its being injected in the general piping.

In installations with a higher degree of automation, the lime is dosed depending on the EC of the slurry. In these cases the EC is a better indicator of the quality of the dosing than pH.

The slurry is prepared in a concentrator to a maximum 4% $Ca(OH)_2$. It is then sent to the decanter, also known as the saturator, for the removal of impurities. The rate of ascent in the decanter should be around 1.8 m/h and its height at least 3.5 m.

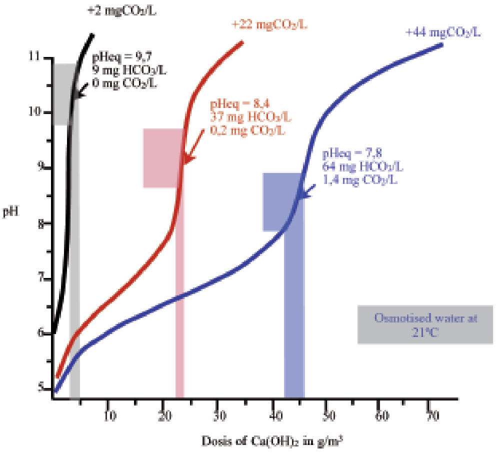

Figure 5.16: Relationship between $Ca(OH)_2$ dosing and pH increase for desalinated waters with three levels of CO_2 content. Adapted from Mutschmann and Stimmelmayr (2002).[15]

Figure 5.18 shows a photograph of a typical lime slurry-based remineralisation installation. There are normally serious compacting problems in the lime silo, due to the tendency of the lime to absorb water and stick to the walls and stirring blades of the silo.

Consequently, it is important to maintain the humidity in the silo as low as possible and to reduce the periods between recharging operations in order to facilitate renewal.[16]

The fundamental difference, as regards costs, with respect to the process of remineralisation by calcite bed filtering is that the process with $Ca(OH)_2$ requires twice the CO_2, in addition to frequent recharging and control of obstruction by precipitation of calcium carbonate.

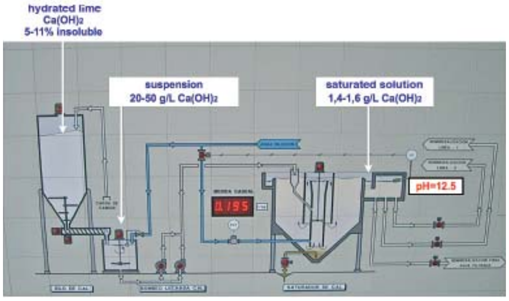

Figure 5.17: Schematic representation of a remineralisation installation with lime slurry preparation and dosing with CO_2.

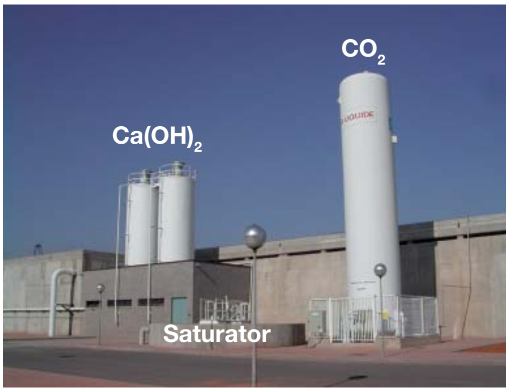

Figure 5.18: Plant for treatment with $Ca(OH)_2$ and CO_2.

5.3.1 $Ca(OH)_2$ quality

Apart from the certificate for use in drinking water supply, the lime should have the composition indicated in Table 5.3

TABLE 5.3: *RECOMMENDATION REGARDING THE QUALITY OF LIME ($CA(OH)_2$). VALUES IN % BY DRY WEIGHT.*

Parameter	*Recommended value*
Richness	*96-97%*
Granulometry:	*90μm*
Soluble $Ca(OH)_2$	*> 87% by weight*
Inert residue	*<10% by weight*
$CaCO_3$	*> 5% by weight*
As	*< 3% by weight*
Cd	*< 1% by weight*
Cr	*< 16% by weight*
Ni	*< 2% by weight*
Pb	*< 5% by weight*
Sb	*< 1% by weight*
Se	*< 1% by weight*
Fe	*< 1% by weight*
Bulk density	*< 0.6 t/m^3*

5.4 Conclusions

Analysis of the remineralisation techniques shows that the calcite bed and lime slurry techniques are both highly developed. The lower CO_2 consumption of the calcite bed technique and the lower degree of complexity of this process point to its being a more stable technique for the remineralisation of desalinated waters than dosing with lime slurry.

CO_2 dosage should be in down flow with a descending speed of about 0.12 ± 0,02 m/s in order to avoid dragging the bubbles or over dosage. The injection pressure should be about 0.25 bars greater than that of water.

The time required for the dissolution of CO_2 can be reduced considerably when using the criteria outlined in the preceding paragraph. Usually about 5 seconds are required for a dissolution of CO_2 from 10 to 40 mg/L using the above criteria.

In any case, the dosage of CO_2 in horizontal pipe should be avoided.

Decreases in temperature reduce the speed of the reactions intervening in remineralisation. In the case of calcite beds, the contact time required to achieve adequate remineralisation increases from 10 to 14 minutes with a decrease in water temperature from 28ºC to 14ºC.

5.5 References

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6. PROCEDURE FOR THE SAMPLING, CONSERVATION AND ANALYSIS OF DESALINATED AND REMINERALISED WATERS

6.1 Introduction

Generally speaking, the waters from reverse osmosis plants have a very low content in bicarbonates (1-3 mg HCO_3^-). As a result, even minor changes in the CO_2 content lead to substantial variations in pH. Thus, for example, a normal permeate at 17ºC with a pH of 5.8 contains around 3.6 mg CO_2/L. The same permeate when aerated loses CO_2 to 1.1 mg/L, as a result of which the pH changes to 6.3.

CO_2 acts as an acid. When water absorbs CO_2 the pH decreases and when it loses CO_2 the pH increases. Under normal pressure and temperature conditions the CO_2 content of the air is around 0.56 mg CO_2/L.

CO_2 loss or absorption may occur both during sampling and during sample conservation due to the presence of an air chamber inside the bottle, or the analytical procedure when this entails some sort of stirring.

In remineralised waters the values of HCO_3^- are normally around 60-70 mg/L. This makes the water better buffered, as a result of which it is less likely to undergo major changes during sampling. However, in those cases in which the water contains excess CO_2 after remineralisation, there may be a loss if the analytical process used involves stirring. In these cases the measured pH will probably be higher than the actual value. In order to minimise CO_2 loss or absorption and make the results obtained by different laboratories as uniform as possible, it is recommended that the following procedure be used for sampling, the conservation of samples and analysis of the pH of desalinated and remineralised waters.[1,2]

6.2 Material

- *A plastic bucket with a capacity of some 15 litres*
- *A clean and dry glass bottle with a wide neck and a leaktight seal (preferably a laboratory item).*
- *Three or four metres of flexible, thick-walled hose.*

6.3 Sampling

1. *Connect the flexible hose directly to the sampling tap of the permeate or remineralised water and run it to the bottom of the bucket. Open it and allow the bucket to fill gradually. Avoid the water coming out at excessive pressure and causing turbulence.*
2. *Fill the bucket and allow it to overflow for approximately 1 minute.*
3. *Insert the bottle gradually to the bottom of the bucket with the opening facing downwards and then turn it slowly for it to fill gradually.*
4. *Wait for the bottle to fill completely and for all the air to come out.*
5. *Close the bottle under water and without leaving any bubbles inside.*
6. *Remove the bottle from the bucket and turn it to check that there is no air inside. If there is, repeat the sampling process.*

If no bucket is available and the sample has to be taken directly from the outlet tap, do this with little flow and leaving a positive meniscus at the neck of the bottle in order to prevent air being left inside the bottle on closing.
Figure 6.1 illustrates the sampling procedure.

6.4 Conservation of sample

- *If analysis is performed immediately or within 1 hour, attempt to keep the bottle at a temperature slightly lower than the permeate at the moment of sampling. Do not expose it to sunlight or allow it to heat up.*
- *If the samples are to be stored for analysis some other day, the samples should be kept at a temperature slightly lower than the permeate at the moment of sampling*

6.5 Labelling of sample

- *Include the place, date and time on the label, along with any specific observations such as "in situ" measurements of temperature, EC and pH.*
- *It is advisable to include the name of the person responsible for sampling and transport to the laboratory, in order to keep a chain of custody protocol.*

6.6 Laboratory analysis procedure

- *Remove the bottle from the refrigerator and leave it for the time required for it to reach a temperature slightly lower than the original permeate.*
- *Do not shake the bottle during this period but simply turn the bottle a couple of times.*
- *For the measurement of pH, open the bottle – which if possible should have a wide neck – and insert the pH probe directly.*
- *Stir the probe or bottle very slightly 4 or 5 times. Do not insert any stirrer in the bottle or stir it too strongly. The aim is for the CO_2 content not to be altered.*
- *Allow the reading to stabilise for approximately 30 seconds and then take down the reading. Do not wait any longer since both the CO_2 and the pH will vary.*
- *The pH meter should be calibrated not only at 4 and 7 but also at 9.5 or 10.4*
- *Alkalinity should be measured following SM-2320B*[5]

The following is a summary of the SM-2320B method for measuring alkalinity by titration.

In the analysis of alkalinity by titration, the final pH value of a sample depends on the total alkalinity (TAC). That is:

1. *For samples of values lower than 20 mg $CaCO_3$/L, the formula to be applied is the following:*

$$\text{Alkalinity, mg } CaCO_3/L = \frac{(2B-C) \times N \times 50\,000}{\text{ml sample}}$$

Where:
B: ml titrant to pH 4.6.
C: ml titrant for pH 4.3 (0.3 pH units difference).
N: normality of standard acid

2. *For sample values greater than 20 mg $CaCO_3$/L, the formula applied is as follows:*

$$\text{Alkalinity, mg } CaCO_3/L = \frac{(A \times N \times 50{,}000)}{\text{ml sample}}$$

Where:

A: ml standard acid used to reach the final pH
N: normality of standard acid

And where the final pH depending on the values of alkalinity, are:

- *For samples with 20-30 mg $CaCO_3$/L, the final pH is 4.9.*
- *For specimens with 30-150 mg $CaCO_3$/L, the final pH is 4.6.*
- *For samples with 150-500 mg $CaCO_3$/L, the final pH is 4.3.*

6.7 Recommendations to be taken into account

- *Bottles that may have contained gassy water should never be used. This is important because it has been observed that the CO_2 is absorbed in some way by the walls of the bottle, altering pH measurements.*
- *Bottles should be below ambient temperature prior to being used for "in situ" data acquisition.*

6.7 References

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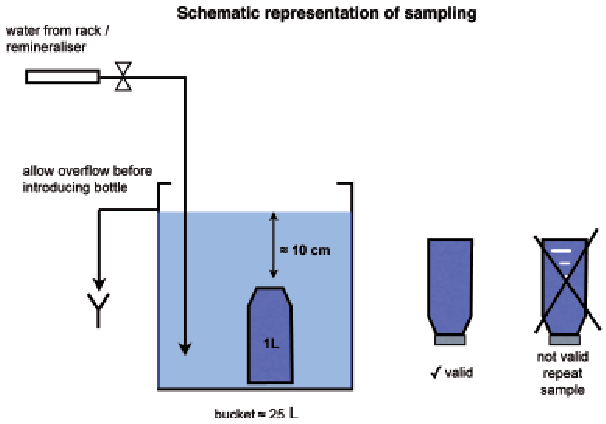

Figure 6.1: Schematic representation of sampling procedure for desalinated and remineralised waters

7. MIXES OF REMINERALISED AND DESALINATED WATERS

7.1 Introduction

The idea of mixing desalinated and remineralised waters is often proposed with a view to reducing the size of the remineralisation unit while maintaining the criterion of LSI > - 0.5.

This chapter analyses different options using two mixing simulation programmes previously validated with actual data obtained in the laboratory. Then, using the one that best predicts the results, different proportions of desalinated water and remineralized are analyzed. Finally, a study of mixtures of permeate with fresh water is also carried out.

7.2 Materials and methods

Two mixing programmes have been used: Water-Pro[1] and Softmix[2]. The data for validation were compiled from the archives of the Mancomunidad de los Canales del Taibilla (MCT) laboratory in Cartagena (Spain).

7.3 Results of mixing simulation programme validation

The results of validation of the mix using the Water-Pro programme are shown in Figures 7.1 to 7.4 for calcium, alkalinity, pH and LSI, respectively.

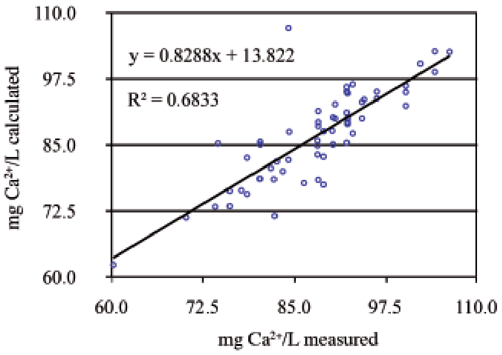

Figure 7.1: Relationship between measured and calculated calcium for MCT water mixes using Water-Pro.

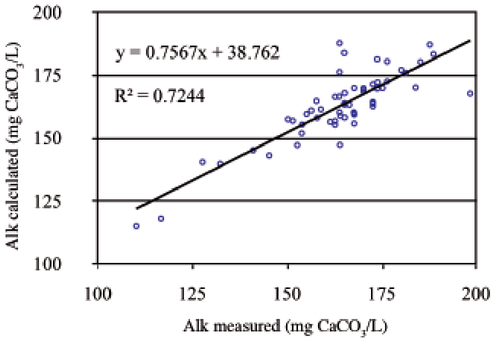

Figure 7.2: Relationship between measured and calculated alkalinity for MCT water mixes using Water-Pro.

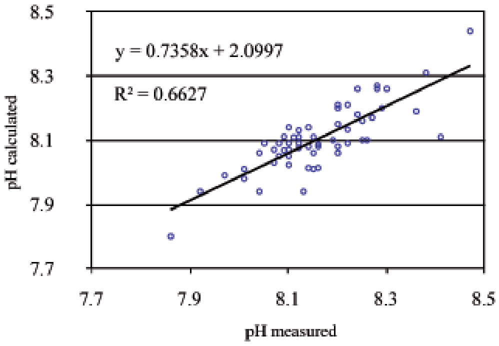

Figure 7.3: Relationship between measured and calculated pH for MCT water mixes using Water-Pro.

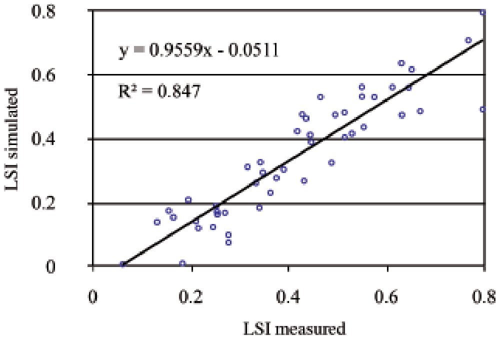

Figure 7.4: Relationship between measured and calculated LSI for MCT water mixes using Water-Pro.

The results point to an acceptable correlation, especially as regards LSI (Figure 7.4).

For their part, the analyses performed using the Softmix programme show a lesser correlation. The data for LSI are presented by way of an example (Figure 7.5).

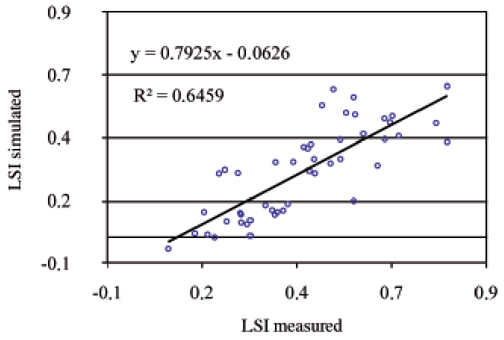

Figure 7.5: Relationship between measured and calculated LSI for MCT water mixes using SoftMix.

In view of these results, the Water-Pro programme has been selected for the study of mixes with desalinated waters.

7.5 Study of mixes of desalinated and remineralised water

The simulation has been performed in order to determine what percentage of desalinated water may be mixed with fully remineralised water (LSI = 0) without the LSI dropping to below -0.5, the lower limit established in Spanish Royal Decree 140/2003.

Table 7.1 summarises the results of the simulation. Figure 7.6 shows the same data graphically.

According to this simulation it may be concluded that if more than 15% of desalinated water is added to a remineralised water with 60 mg $CaCO_3$/L of alkalinity, the LSI will drop to below -0.5.

These results refer to a system that is not open to the atmosphere, as a result of which for open systems the loss of CO_2 may allow the percentage of desalinated water to increase slightly.

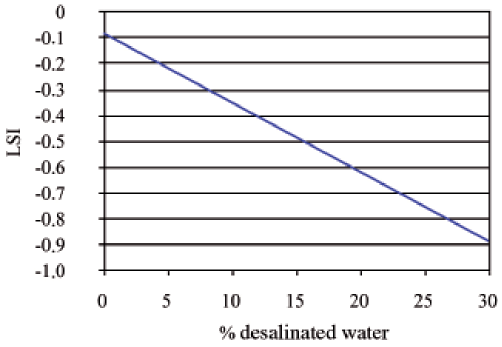

Figure 7.6: Value of LSI depending on percentage of desalinated water added to remineralised water with 60 mg $CaCO_3$/L alkalinity.

***TABLE 7.1:** VARIATION IN THE COMPOSITION OF THE MIX OF REMINERALISED WATER AND NON-REMINERALISED DESALINATED WATER DEPENDING ON THE PERCENTAGE OF DESALINATED WATER IN THE MIX FOR A CLOSED SYSTEM (NOT OPEN TO THE ATMOSPHERE)*

	% desalinated water							
Parameter	0%	5%	10%	15%	20%	25%	30%	100%
STD, mg/L	300	295	290	285	280	275	270	200
Alk, mg $CaCO_3$/L	60.00	57.20	54.30	51.50	48.60	45.80	42.90	3.00
pH	8.23	8.14	8.05	7.96	7.87	7.78	7.70	6.10
Ca^{2+}, mg/L	22.00	20.90	19.90	18.80	17.70	16.70	15.60	0.60
T, ºC	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Cl^-, mg/L	156.00	156.00	156.00	156.00	156.00	156.00	156.00	156.00
Mg^{2+}, mg/L	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
SO_4^{2-}, mg/L	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
CID, mg/L	14.44	13.82	13.20	12.58	11.96	11.34	10.71	2.03
CO_2, mg/L	0.67	0.79	0.93	1.09	1.26	1.45	1.65	4.76
LSI	-0.09	-0.21	-0.35	-0.48	-0.62	-0.75	-0.89	-5.03

7.6 Study of the mix of desalinated water and continental water

Table 7.2 shows the results of the simulation using Water-Pro of a mix of a continental water and a non-remineralised desalinated water.

According to these data, up to 50% non-remineralised desalinated water may be added without the LSI dropping to below -0.5.

Again, these data refer to a closed system, for which reason in a system open to the atmosphere, with the possibility of excess dissolved CO_2 being eliminated, the percentage of desalinated water in the mix might increase by a few points.

TABLE 7.2: *VARIATION IN THE COMPOSITION OF THE MIX OF CONTINENTAL WATER AND NON-REMINERALISED DESALINATED WATER DEPENDING ON THE PERCENTAGE OF DESALINATED WATER IN THE MIX FOR A CLOSED SYSTEM (NOT OPEN TO THE ATMOSPHERE)*

Parameter	Continental water	Non-remineralised desalinated water	Mix (closed system not open to the atmosphere)
% of Total Flow	50%	50%	100%
STD, mg/L	878	412	678
Alk, mg $CaCO_3$/L	192.00	2.00	110.90
pH	8.48	5.40	7.28
Ca^{2+}, mg/L	104.00	1.40	59.90
T, ºC	19.00	22.10	20.30
Cl^-, mg/L	133.00	116.00	125.70
Mg^{2+}, mg/L	54.00	2.30	31.80
SO_4^{2-}, mg/L	300.00	4.50	172.90
LSI	1.11	-4.02	-0.45

7.7 References

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