

## Indirect calculation of Langelier saturation index and sodium adsorption ratio for remineralised waters from data on electrical conductivity and pH prior to and following remineralisation

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### ABSTRACT

This article shows the results obtained about the possibility of the indirect calculation of SDI and sodium adsorption ratio (SAR) based on electrical conductivity at 25°C ( $EC_{25}$ ) and pH data prior to and following remineralisation, using the quotient between  $EC_{25}$  and alkalinity (Alk). The importance of this work is to propose a new calculation method which is required to estimate with certain precision the increase in alkalinity and hardness that has been achieved with remineralisation. It is justified to investigate the relationship between the alkalinity values and the remineralised water. The novelty of this work is to have been done based on real data taken from different desalination plants as well as theoretical calculations based on the contribution of each ion to the conductivity of the water. For instance, Alk(0) ranges are from 0.5 to 2.8 mg  $CaCO_3/L$  for values of  $EC_{25}(0)$  of between 250  $\mu S/cm$  and 700  $\mu S/cm$  respectively. 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 Langelier saturation index LSI(r) calculation method should be SM-2330. This procedure allows LSI(r) to be estimated with an accuracy in between of +0.05 and -0.05. According to the study performed and 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 electrical conductivity should be within the range 85–97. The mean value of SAR or sodium absorption rate of desalinated water is around 9. This point to water that can cause damage not only to the soil but also to some crops due to an excess of sodium over calcium and magnesium. This aspect should therefore be corrected. Either with a remineralization or by adding calcium and magnesium directly with fertilizers. 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.

**Keywords:** Remineralisation; Reverse osmosis; Desalination; Langelier saturation index; Sodium adsorption ratio; Electrical conductivity

### 1. Introduction

The Langelier saturation index (LSI) is calculated from the values of electrical conductivity or total dissolved solids, calcium, alkalinity, pH and temperature. In practice, the conductivity, pH and temperature are calculated.

In practice, in most desalination plants, calcium is measured continuously, but not because it requires a specific and more expensive probe [1–3].

The alkalinity on the other hand cannot be analyzed in continuous since commercial equipment does not exist that allows it. In some desalination plants, total inorganic carbon

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Table 1

Theoretical composition of desalinated water in proportion to decreasing  $CE_{25}$  values obtained using criteria explained in the text

$CE_{25}$ , $\mu\text{S}/\text{cm}$	700	600	500	400	300	200	100
pH	6.2	6.2	6.2	6.2	6.2	6.2	6.2
$\text{Ca}^{2+}$ , mg/L	1.67	1.44	1.22	0.99	0.77	0.54	0.31
$\text{Mg}^{2+}$ , mg/L	2.87	2.49	2.10	1.71	1.32	0.93	0.54
$\text{Na}^{+}$ , mg/L	108.64	93.15	77.66	62.17	46.68	31.19	15.70
$\text{K}^{+}$ , mg/L	5.17	4.47	3.77	3.07	2.37	1.67	0.97
$\text{Cl}^{-}$ , mg/L	205.31	175.28	145.25	115.22	85.19	55.16	25.13
$\text{SO}_4^{2-}$ , mg/L	4.71	4.07	3.43	2.80	2.16	1.52	0.89
$\text{HCO}_3^{-}$ , mg/L	2.17	1.88	1.58	1.29	1.00	0.70	0.41

meters have been installed, which can be correlated with alkalinity, but they are expensive equipment and therefore their implementation is limited. Therefore, the importance of this work is to propose a new calculation method which is required to estimate with certain precision the increase in alkalinity and hardness that has been achieved with remineralisation [1,3–5].

Therefore, it is justified to investigate the relationship between the alkalinity values and the remineralised water. The novelty of this work is to have been done based on real data taken from different desalination plants as well as theoretical calculations based on the contribution of each ion to the conductivity of the water [1,6–9].

It is evident from these equations that the increase in electrical conductivity produced by remineralisation is directly proportional to the increase in alkalinity since it has only increased in bicarbonate and calcium content. It should also be considered that the impact of the increase in alkalinity is not the same in desalinated water with low conductivity, such as low sodium chloride content, as in desalinated water with high conductivity, such as high sodium chloride content, so this aspect must be considered. In processes where hydrochloric acid or sulphuric acid is added instead of carbon dioxide the proportions are different, but these cases have been considered in this article [10–16].

## 2. Material and methods

Desalinated water is a solution with around 72% of ClNa. Thus, the conductivity of desalinated water is directly proportional to the increase in chloride and sodium.

We must define the following parameters to be considered in the article [2].

LSI: Langelier saturation index

SAR: Sodium adsorption ratio

EC: Electrical conductivity

Alk: Alkalinity

About the indirect calculation of SDI and SAR based on electrical conductivity at 25°C ( $EC_{25}$ ) and pH data prior to and following remineralisation (depending on the permeate  $EC_{25}$ ):

$$\frac{\Delta EC_{25}}{\Delta \text{Alk}} = 1.55 - 1.75 \quad (1)$$

where:

$$\Delta \text{Alk} = \text{Alk}(r) - \text{Alk}(0) \quad (2)$$

and

$$\Delta EC_{25} = EC_{25}(r) - EC_{25}(0) \quad (3)$$

For instance,  $\text{Alk}(0)$  ranges are from 0.5 to 2.8 mg  $\text{CaCO}_3/\text{L}$  for values of  $EC_{25}(0)$  of between 250  $\mu\text{S}/\text{cm}$  and 700  $\mu\text{S}/\text{cm}$  respectively. The  $\text{Ca}(r)$  value remineralised water may be calculated from the ratio  $\text{Ca}(r) = \text{Alk}(r)/2.5$ . The values of  $\text{pH}(r)$  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 SM-2330 [5].

This procedure allows LSI(r) to be estimated with an accuracy in between of +0.05 and –0.05. According to the study performed and to achieve the optimum levels indicated in Table 1, the increase in alkalinity should be at least 55 mg  $\text{CaCO}_3/\text{L}$ . This implies that the increase in electrical conductivity should be within the range 85–97.

Real data analyzed in the laboratory have been used to estimate the value of the ratio increase in electrical conductivity broken down by an increase in alkalinity. On the other hand, the value of the ratio has been obtained by using, firstly, a model of remineralisation with calcite with different levels of carbon dioxide dosage and secondly by calculating the electrical conductivity of the remineralised water using the ionic contribution method published in the standard methods [1,8–10].

In this article is defined a methodology as the water that comes directly from the desalination process. 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 paper come all from seawater desalination plants. This work includes, first, an extensive bibliographical survey on these issues with special attention paid to quality standards and analytical methods [8,9].

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 based on the

increases in electrical conductivity (EC) and pH caused by remineralisation [12–15].

The LSI is calculated from the values of electrical conductivity or total dissolved solids, calcium, alkalinity, pH and temperature. In practice, the conductivity, pH and temperature are calculated. In practice, in most desalination plants, calcium is measured continuously, but not because it requires a specific and more expensive probe.

LSI and the re-mineralised water can be calculated from the increase in electrical conductivity produced by the re-mineralisation using the quotient:

$$\frac{\Delta CE}{\Delta Alk} = 2.976E-7 \times [CE_{25}(0)]^2 - 0.0006 \times CE_{25}(0) + 1.84 \quad (4)$$

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 calcium value of the mineralised water can be calculated from the ratio of calcium to alkalinity of 2.5 points. The pH and temperature values should be taken on site by means of the measuring equipment installed on the line. Once all the parameters have been obtained, it is obtained the calculation method of the LSI [1].

This procedure allows to estimate the LSI and with an approximation in between +0.5 and -0.5.

The mean value of SAR or sodium absorption rate of desalinated water is around 9. This points to water that can cause damage not only to the soil but also to some crops due to an excess of sodium over calcium and magnesium. This aspect should therefore be corrected. Either with a re-mineralization or by adding calcium and magnesium directly with fertilizers.

### 3. Results and discussion

In this section it is shown the results obtained of this study and the discussion of them accordingly. Fig. 1 presents the relationship between the permeate EC and the value of the ratio.

Fig. 2 includes the results of the calculations of the increase in electrical conductivity broken down by the increase in alkalinity obtained from the real data of three desalination plants, and by calculating the ionic partition to the electrical conductivity for three typical remineralised waters but with increasing levels of electrical conductivity.

For the simulation of the quality of the remineralised water, it has been considered that the water reaches a LS and equal to zero from a permeate with a pH of 6.2 and where the values of sodium potassium and chlorine vary proportionally according to the electrical conductivity following the relationships in Fig. 3.

The values of magnesium, calcium and sulphate were calculated according to the following. Table 1 illustrates the starting composition of these desalinated waters.

From this, 20.27 and 35 mg of carbon dioxide per liter have been dosed and the composition of the remineralised water has been calculated by mathematical simulation.

The theoretical electrical conductivity value of the mineralized water was calculated according to the criteria of the SM-2010 [1,3,7].

The theoretical results presented in Fig. 1 for the three levels of electrical conductivity: 300, 500 and 700 uS/cm point to a clear reduction in the quotient with an increase in conductivity.

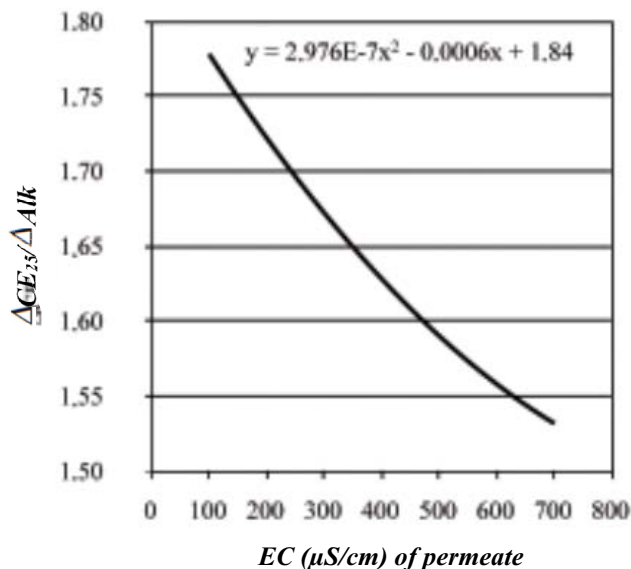


Fig. 1. Relationship between the EC<sub>25</sub> of the permeate and the ratio  $\Delta CE_{25}/\Delta Alk$  for the water remineralised up to pH 8.2.

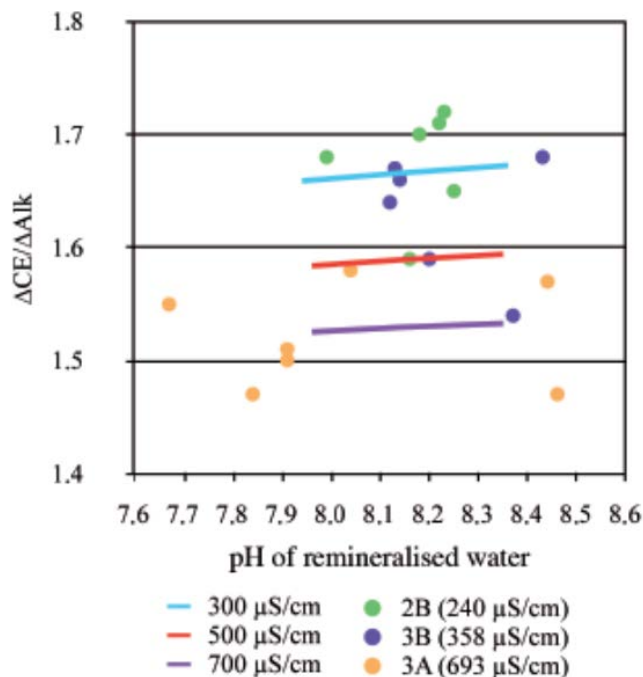


Fig. 2. Relationship between the pH of remineralised water and the quotient  $\Delta CE_{25}/\Delta Alk$ . Lines for 300, 500 and 700 uS/cm have been obtained by mathematical simulation 1,2.

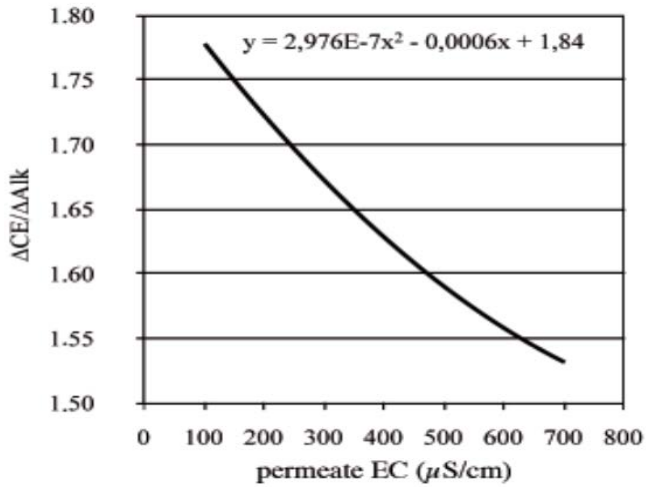


Fig. 3. Relationship between permeate EC and the quotient  $\Delta EC_{25}/\Delta Alk$  for waters remineralised up to pH 8.2. The line has been defined using a mathematical simulation of remineralisation 1,2.

As can also be seen in Fig. 1, this effect corresponds, although in a rather diffuse manner, to the data obtained from different desalination plants [3,5–7].

To analyze the impact of electrical conductivity on the value of the quotient, the theoretical study has been extended to obtain the relationship between the electrical conductivity of the permeate and the coefficient value [1,3]. Fig. 2 illustrates this relationship, using only the dosage value of 27 mg of carbon dioxide per liter, which corresponds to an equilibrium pH of 8.14 [1].

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

According to Fig. 2:

$$\frac{\Delta CE}{\Delta Alk} = 2.976E-7 \times [CE_{25}(0)]^2 - 0.0006 \times CE_{25}(0) + 1.84 \quad (5)$$

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 [7].

The results are shown in Table 1 and the relationship between the calculated and actual LSI values is included in Fig. 4.

### 3.2. Indirect calculation of SAR

The correlation established for desalinated water should be used for the calculation of the SAR [1].

$$Na(r)(mg/L) = Na(0)(mg/L) = 0.1549 \times EC_{25}(0) + 0.2137 \quad (6)$$

The following may be assumed in the case of magnesium:

$$Mg(r)^{2+} = Mg(0)^{2+} = 1.8 \times mg K^+/L \quad (7)$$

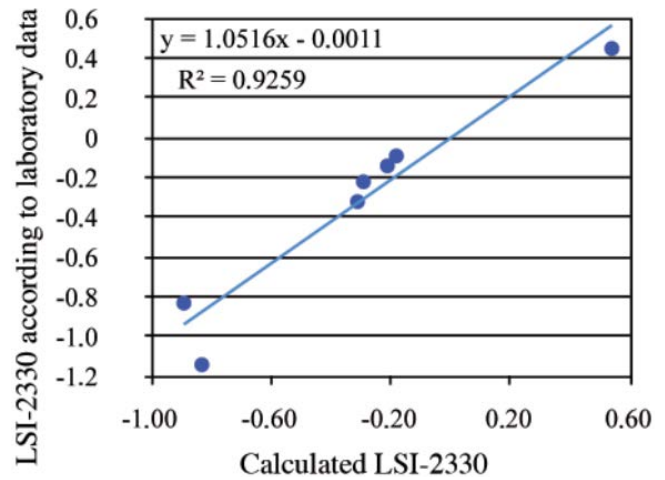


Fig. 4. Relationship between LSI calculated in accordance with the criteria of paragraph 3.1 and the laboratory data.

or

$$Mg(r)^{2+} = Mg(0)^{2+} = 2.5 \times mg K^+/L \quad (8)$$

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

$$Ca^{2+}(r) = \frac{Alk(r)}{2.5} \quad (9)$$

### 3.3. Sampling and analytical considerations

As noted above, it is important in sampling to avoid loss of carbon dioxide. It is therefore advisable to optimize the sampling in this respect by avoiding airing. pH and temperature samples should preferably be taken online. Otherwise, it is recommended to follow the protocol proposed above. It is advisable to reference the electrical conductivity measurements at 25°C [9–12].

Finally, it is always recommended to make the alkalinity measurements following the procedure SM-2320B [7].

## 4. Conclusions

The results obtained indicate that the LS and the mineralised water can be calculated from the increase in electrical conductivity produced by the re-mineralisation using the quotient:

The calcium value of the mineralised water can be calculated from the ratio of calcium to alkalinity of 2.5 points. The pH and temperature values should be taken on site by means of the measuring equipment installed on the line. Once all the parameters have been obtained, the calculation method of the LS and must be the SM-2330 [5].

This procedure allows to estimate the SL and with an approximation in between +0.5 and –0.5.

According to the study carried out, and to reach the optimal levels indicated in Table 1, the increase in alkalinity must be at least 55 mg of calcium carbonate per litre.

This implies that the increase in electrical conductivity caused by the re-mineralisation should be in the range:

$$\Delta EC_{25} = 85 - 97 \quad (10)$$

The following may be assumed to calculate the SAR(r):

$$Ca(r) = \frac{Alk}{2.5} \quad (11)$$

$$Mg(r) = 2.5 \text{ mg/L} \quad (12)$$

$$Na(r)(\text{mg/L}) = 0.1549 \times EC_{25}(0) + 0.2137 \quad (13)$$

The sampling conditions should be optimized to avoid the loss of carbon dioxide and to obtain pH and temperature values as close as possible to the operating conditions before and after the remineralization system.

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