Estimation of stream compositions in reverse osmosis seawater desalination systems

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ABSTRACT

An algorithm was developed for estimating salinity and compositions of the major constituents in streams of seawater desalination systems using the reverse osmosis. The algorithm implementation is based on the seawater equation state and, except for the salinity (in which it is always valid), it is applicable when the ratio between the composition of an ionic constituent in a stream and its salinity is constant. The study case examined was the Unit 1 of the Desalination Plant of Porto Santo. The solution of the algorithm equations, using the Excel spreadsheet, enabled a good supervising of the salinities and chloride and sodium ionic concentrations in the feed and permeates streams.

Keywords: Reverse osmosis; Electrical conductivity; Salinity; Seawater

1. Introduction

The increase in water demand and the continuous search of freshwater resources not yet exploited have aided seawater in becoming an important source for potable water supply. However, for obtaining potable water from seawater is necessary to separate significant fractions of their major constituents.

Reverse osmosis (RO) is one of the most promising techniques for seawater desalination, which has been increasingly used as feasible technology for water treatment around the world taking advantage of the economy of scale [1]. In the RO process, the membranes based on semi-permeable polymeric materials are a selective barrier to the salt flux, hence causing the production of a permeate stream susceptible to be considered as potable water.

The World Health Organization (WHO) did not establish in the Guidelines for Drinking-water Quality criteria for characterizing potable waters in terms of total

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dissolved solids (TDS), and chloride and sodium ionic concentrations [2]. However, this document recognizes that values higher than 1200, 250 and 200 mg/L for TDS, Cl^- and Na^+, respectively, can cause some objection from consumers and give water a disagreeable taste.

The three values previously cited can be used as reference compositions in the permeate stream of RO desalination systems. For the ionic species, it is more difficult to assure those values, in particular for the chloride ion. This may be explained considering that monovalent ions are permeated more easily than other through reverse osmosis membranes since these ions together are the most abundant in seawater.

In order to simplify, the homogeneous phase of the seawater can be considered as a mixture formed by water and 11 major dissolved constituents (assumed in this paper as equivalent to the TDS), which represent 99.99% of all of its solutes [3]. The seawater salinity is very variable and strongly influenced by climacteric factors, coastal habitats, sea streams, pollution, etc. The compositions of the principal constituents in the seawater are nearly constants (see Table 1). Theoretically, it is only

Table 1
Ionic compositions in seawater

Ion	Ions in seawater, %	Ions by weight, %	Cumulative, %
Chloride (Cl$^-$)	18.98	55.04	55.04
Sodium (Na$^+$)	10.556	30.61	85.65
Sulphate (SO$_4^{2-}$)	2.649	7.68	93.33
Magnesium (Mg^{2+})	1.272	3.69	97.02
Calcium (Ca^{2+})	0.4	1.16	98.18
Potassium (K$^+$)	0.38	1.1	92.28
Bicarbonate (HCO$_3^-$)	0.14	0.41	99.69
Bromide (Br$^-$)	0.065	0.19	99.88
Boric acid (H$_3$BO$_3$)	0.026	0.07	99.95
Strontium (Sr^{2+})	0.013	0.04	99.99
Fluoride (F$^-$)	0.001	0	99.99

Table 2
Electrical conductivity and correlation factor between salinity and electrical conductivity of waters in RO systems, adapted from [4]

Water	$K_{25°C}$, μS.cm^{-1}	k, ppm.cm.μS^{-1}
Permeate (for ultrapure water)	1–10	0.5
Permeate (for potable water)	300–800	0.55
Seawater	45,000–60,000	0.7
South Pacific seawater	<51,660	0.694–0.699
Gran Canaria Atlantic Seawater	53,280	0.704
Sardinia Mediterranean seawater	57,240	0.714
Concentrate	65,000–85,000	0.75

necessary to measure one of them, typically the chloride composition, to determine of other constituent or its salinity [3].

For the assessment of the performance of RO systems, a permanent supervision of key variables is required, such as the recovery ratio and the productivity, related with the quality and quantity of each stream in the process. In the feed stream, certain operating parameters, especially the pressure, can be adjusted in order to maximize the recovery or to improve the process efficiency. With respect to the permeate stream, these adjustments allow to match their characteristics with the production target and the legal requirements of the water quality.

Information on the composition of the streams in RO processes it is difficult to get in real-time. For seawater, this difficulty is aggravated by the variety of ions and other components existent in solution. Thus, the advantages are evident in applying strategies to feasibly estimate in real-time the desired compositions.

The standard procedure adopted for the supervision of the salinity of RO streams is based on the monitoring of the electrical conductivity, K. In practice, in-situ measurements are made with conductivity meters that incorporate a compensation system of the temperature to 25°C. The membrane manufacturers usually supply coefficient values, k, to correlate the salinity, S_t, and the electrical conductivity, K, of aqueous solutions as shown in Table 2. This procedure originates non-rigorous estimates of the respective salinities

In order to characterize completely the chemical composition of the streams, the performing of periodical analyses in the laboratory is needed. Sometimes the time delay between the sampling and the knowledge of the results is significant, corresponding to several hours or days. This work presents a strategy to estimate, "on-line", the salinity and the compositions of the principal constituents of the streams in desalination systems by RO.

2. Theory

The most usual and feasible method for the determination of the salinity, S_t, is based on the measurements of electrical conductivity [5]. The Practical Salinity Scale (PSS) can be used to compute the salinity of the seawater, this scale being valid for salinities varying between 2 and 42 [6]. The PSS is defined in terms of the ratio K_{15} of the electrical conductivity of the seawater sample at a temperature of 15°C and a pressure of one standard atmosphere to that of a potassium chloride (KCl) solution. The PSS can be extended to solutions of lower salinity, between 0 and 40, using Eq. (1) [5]:

$$S_t = S_T - \frac{0.008}{1+1.5X+X^2} - \frac{0.005 f(T)}{1+Y^{1/2}+Y^{3/2}}. \tag{1}$$

where S_T is the salinity calculated by Eq. (2); $f(T) = (T-15)/[1+0.0162(T-15)]$; $X = 400\,R_T$; $Y = 100\,R_T$; and R_T is the conductivity ratio defined by Eq. (4).

$$S_T = a_0 + a_1 R_T^{0.5} + a_2 R_T + a_3 R_T^{1.5} + a_4 R_T^2 + a_5 R_T^{2.5} + \Delta S_T \tag{2}$$

where ΔS_T is given by Eq. (3); a_i and b_i are constants whose values are indicated in Table 3.

$$\Delta S_T = \frac{(T-15)}{1+0.0162(T-15)}$$
$$\left(b_0 + b_1 R_T^{0.5} + b_2 R_T + b_3 R_T^{1.5} + b_4 R_T^2 + b_5 R_T^{2.5}\right) \tag{3}$$

$$R_T = K(S_t, T, 0)/K(35, T, 0) \tag{4}$$

where $K(S_t, T, 0)$ is the electrical conductivity of a solution

Table 3
Constant values of some of the above equations

a_0	a_1	a_2	a_3	a_4	a_5	$\sum a_i$
0.008	−0.1692	25.3851	14.0941	−7.0261	2.7081	35.0000
b_0	b_1	b_2	b_3	b_4	b_5	$\sum b_i$
0.0005	−0.0056	−0.0066	−0.0375	0.0636	−0.0144	0.0000
c_0	$c_1 \times 10^2$	$c_2 \times 10^4$	$c_3 \times 10^7$	$c_4 \times 10^9$	—	—
0.6766097	2.00564	1.104259	−6.9698	1.0031	—	—
d_1	$d_2 \times 10^4$	d_3	$d_4 \times 10^3$	$e_1 \times 10^5$	$e_2 \times 10^{10}$	$e_3 \times 10^{15}$
0.03426	4.464	0.4215	−3.107	2.07	−6.37	3.989

of salinity S_t (or 1000 S_t ppm), at temperature T and atmospheric pressure; $K(35,T,0)$ is the electrical conductivity of a solution of salinity 35 (or 35,000 ppm), at temperature T and atmospheric pressure. R_T may be related to the conductivity ratio, r, through Eq. (5):

$$R_T = r/\left(r_T R_p\right) \tag{5}$$

where

$$r = K(c_t,T,p)/K(35,15,0) \tag{6}$$

$r_T = K(35,T,0)/K(35,15,0)$ is defined through Eq. (7) and $R_p = K(c_t,T,p)/K(S_t,t,0)$ is defined according to Eq. (8).

$$r_T = c_0 + c_1 T + c_2 T^2 + c_3 T^3 + c_4 T^4 \cdot \tag{7}$$

$$R_p = 1 + \frac{p\left(e_1 + e_2 p + e_3 p^2\right)}{1 + d_1 T + d_2 T^2 + \left(d_3 + d_4 T\right)r} \cdot \tag{8}$$

where c_i, d_i and e_i are constants given in Table 3.

An algorithm that incorporates the equations previously presented was developed for correlating the electrical conductivity and the salinity of the streams of RO processes. This algorithm uses as input the conductivity measurements, temperature and pressure of each stream. It is possible to extend the scope of the algorithm application to the calculation of the composition of the major chemical constituents of each stream. For that, it is useful to check from some periodical analyses if the ratios of constituents to salinity are kept constant along the time.

3. Case study: desalination plant of Porto Santo

3.1. Plant description

The plant is located in the Porto Santo Island of the Madeira Archipelago (Portugal) and includes four RO

Table 4
Chemical and physical characteristics of seawater

pH	7.8
Conductivity at 25°C (μS.cm^{-1})	54,870
Total hardness (mg.L^{-1}) CaCO$_3$	6191
Total alkalinity (mg.L^{-1} (CaCO$_3$)	175
Concentration of species (kg.m^{-3}):	
Cl$^-$	20.31
Na$^+$	11.32
SO$_4^{2-}$	2.82
Mg^{2+}	1.36
Ca^{2+}	0.42
K$^+$	0.41
HCO$_3^-$	0.22
TDS	37.01

units with a total capacity of 6800 m^3/d. We have studied Unit 1 with a capacity around 1500 m^3/d. This unit started to run on 6 February 2003 and has operated continuously without any chemical cleaning operation of the membranes in the studied period. The unit utilizes spiral-wound Koch membranes and operates at 50–65 bar. Fig. 1 shows a schematic diagram of some parts of the seawater desalination process in unit 1. It consists of four major components as follows: (1) advanced pre-treatment where untreated water after having been filtered by a sand bed is pumped from four subterranean galleries to the surface; (2) conventional pre-treatment consisting of sulphuric acid dosing and microfiltration with cartridge filters of 5 μm; (3) RO unit composed by 24 pressure vessels in parallel, each one of them containing three spiral-wound Koch membranes, (TFC 28323 SS-465 Magnum) modules; and (4) post-treatment of the permeate.

3.2. Some useful information

The streams were monitored approximately under atmospheric pressure and the conductivities were reported at 25°C. Table 4 shows results from a typical analysis of a seawater sample collected from one sub-
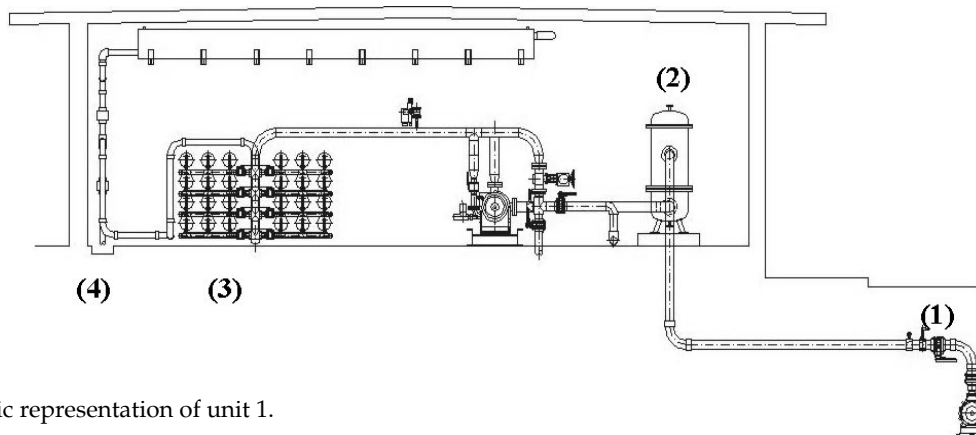
Fig. 1. Schematic representation of unit 1.

Table 5
Chemical and physical characteristics of permeated water

pH	6.9
Conductivity at 25°C (μS.cm^{-1})	606
Total hardness (mg.L^{-1}) CaCO$_3$	8.9
Total alkalinity (mg.L^{-1} (CaCO$_3$)	7.5
Concentration of species (mg.L^{-1})	
$\quad$ Cl$^-$	179
$\quad$ Na$^+$	114
$\quad$ SO$_4^{2-}$	<7
$\quad$ Mg^{2+}	1.7
$\quad$ Ca^{2+}	0.78
$\quad$ K$^+$	4.84
$\quad$ HCO$_3^-$	9.2
$\quad$ TDS	317

terranean gallery in May 5, 2003. Other analyses performed periodically provided similar results.

It should be noted that the chloride and sodium concentrations and the dissolved solids (TDS) in the feed to unit 1 originated compositions as %weight practically coincided with those for seawater indicated in the third column of Table 1. Also the compositions for the pretreated stream using sulphuric acid did not significantly change.

Results from a typical analysis of the permeate stream in unit 1, performed in May 5, 2003, are given in Table 5. The observed ratio of Cl$^-$ or Na$^+$ to *TDS*, in the periodical analysis of the permeate streams, showed maximum relative deviations lower than 2%. The pH permeate was not significantly influenced by these differences.

3.3. Calculation procedure

The steps of the algorithm application for each moment in time, considering the set of all the registrations based online instrument measurements at intervals of 6 h are as follows:

- Calculation of r_T using Eq. (7);
- Calculation of r using Eq. (6). The value of 42,914 mS.cm^{-1} [7] was adopted for $K(35,25,0)$;
- Set R_p equal to 1, since the streams were always monitored under atmospheric pressure;
- Calculation of R_T through Eq. (5);
- Calculation of the salinities for feed and permeate streams using Eqs. (1)–(3). The values found were converted to ppm.
- Calculation of chloride (c_{F1}) and sodium (c_{F2}) ionic concentrations in the feed by multiplying the salinities by 0.5504 and 0.3061, respectively;
- Calculation of chloride (c_{p1}) and sodium (c_{p2}) ionic concentrations in the permeate by multiplying the salinities by 0.56 and 0.36, respectively.

This procedure was implemented in an Excel file containing all the registrations from the conductivity measurements of the streams involved.

4. Results and discussion

Figs. 2 and 3 show the plot of the electrical conductivities of the feed and permeate streams, respectively, which were monitored by on-line measurements during the study. It should be noted that there are great variations of the conductivity generated because of sudden variations of the operating pressure during a short time-step [8]. Ignoring these variations, it can be seen that higher variations relatives to average conductivities occur for the permeate stream due mainly to the effect of temperature on the salt permeability coefficients [8]. From the conductivity data, the salinities and chloride and sodium compositions were estimated by the procedure mentioned before. The results obtained are illustrated in Figs. 4 and 5.

In Fig 4, it can be seen that the feed composition is nearly constant along the time, and the concentrations of the major ionic constituents (Cl$^-$ and Na$^+$) exhibit values similar in magnitude to those indicated in Table 4. The
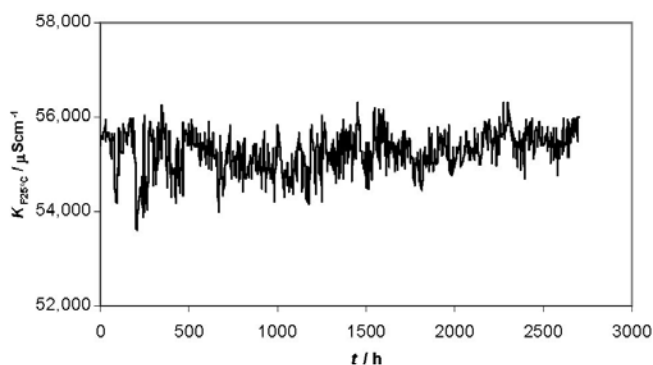
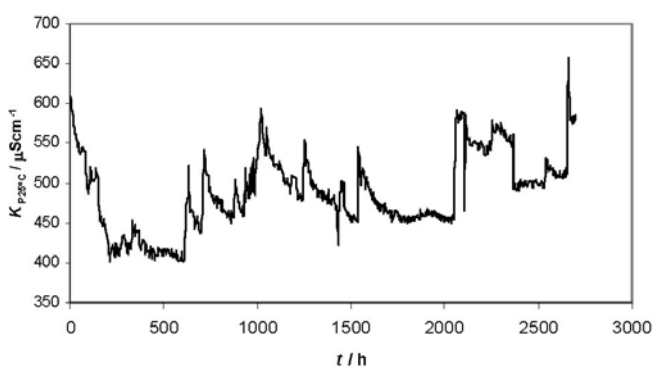Fig. 2. Evolution of electrical conductivity of feed water.

Fig. 3. Evolution of electrical conductivity of permeated water.

Fig. 4. Evolution of salinity (TDS) and ionic concentration of Cl⁻ and Na⁺ in feed water.
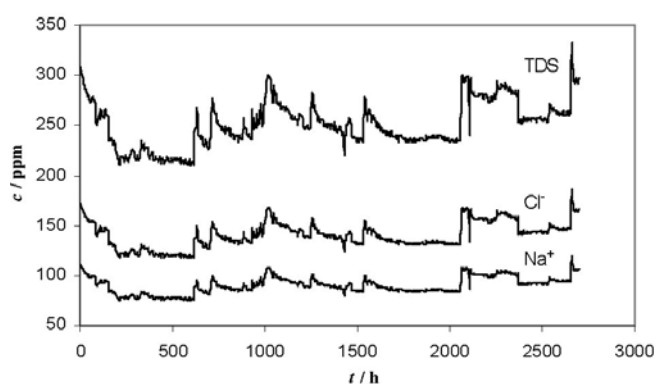
Fig. 5. Evolution of salinity (*TDS*) and ionic concentration of Cl⁻ and Na⁺ in water permeated.

estimates obtained through the application of the algorithm described in Section 3.3 for the values of TDS and compositions of chloride and sodium ions for the analysis previously referred are 36.36, 20.01 and 11.13 kg.m^{-3}, respectively. The respective percentage errors are 1.8, 1.5 and 1.7.

Fig. 5 shows that the quality of the permeate stream was maintained within the reference values indicated in the introduction section. Comparing the concentrations calculated by the algorithm and chemical analysis done periodically to the sodium and chloride ionic compositions in the feed and permeate, as showed for the sample collected in May 5, 2003 (corresponding to time ≈ 2112 h), we find mean relative absolute errors of 2.4% and 4%, respectively, over an extended time period of 454 days relative to that studied from the same starting day of the plant operation. The concentrations of TDS and chloride and sodium ions estimated from the algorithm for the permeate compositions measured (see Table 5) are 307, 172 and 110.5 mg.L^{-1}, respectively. The respective percentage errors are 3.2, 3.9 and 3.1.

The concentrations estimated, as well as other variables that characterized the streams, enabled good estimates of variable and physical parameters of the membrane: osmotic pressures, permeability and rejection coefficients [8].
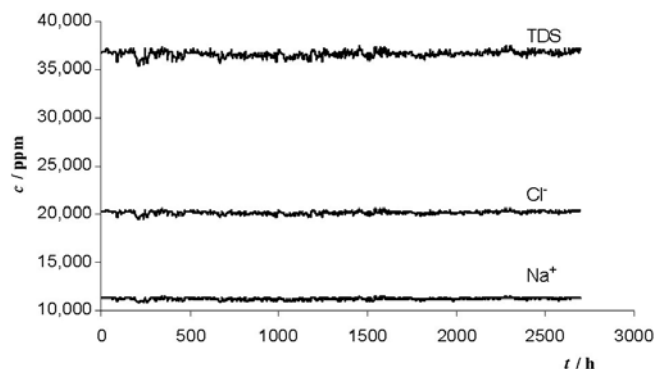
5. Conclusions

Using the algorithm developed in this work, which can be easily implemented using an Excel program and without additional costs for the capital investment of RO units, it is possible to estimate reliably and in real-time, salinities and stream compositions of seawater desalination systems. Therefore, there are advantages in applying the algorithm to supervise, especially permeate quality, which is also important to account for the reliability of the estimates, depending on the degree of accuracy of the measurements from the conductivity meters. This equipment should be calibrated regularly in order to avoid erroneous readings caused by the formation of precipitates [5]. The reliability of data obtained from the electrical conductivities enables reliability of the variables estimated, and, as consequence, a more safe control of the performance of theRO units.

There are no obstacles that hinder the application of the strategy presented for the estimation of the salinity of streams in a RO process. This strategy can be extended to the estimation of the concentration of any other ionic constituent since the ratios of constituents to salinity are maintained constant along the time. We believe that this

condition is valid in several desalination systems using RO, at least for chloride and sodium ions.

6. Symbols

c — Mass concentration, $kg.m^{-3}$
c_t — Salinity (considered equivalent to $TDS \times kg^{-1}m^3$)
k — Correlation factor between salinity and electrical conductivity, $ppm.cm.\mu S^{-1}$
K — Electrical conductivity, $\mu S.cm^{-1}$
p — Relative pressure, dbar
S — Salinity
T — Temperature, °C
TDS — Total dissolved solids, $kg.m^{-3}$

Subscripts

1 — Chloride ion
2 — Sodium ion
F — Feed
P — Permeate

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