THE IMPORTANCE OF OSMOTIC POTENTIAL IN THE BRINE DISCHARGE

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Abstract

To date, the environmental impact of brine discharge from RO plants has been evaluated only in terms of salinity. This alone should not be used to establish discharge limits, as the potential impact on the marine life also depends on the osmotic potential of the brine, not just salinity.

A natural semi-permeable cell membrane makes osmosis an important phenomenon that must be taken into account by all living organisms. Plants use osmosis to increase turgidity, and animal organisms need to control the osmotic pressure to avoid an over inflation and over shrinking of cells.

Turgency and plasmolysis both depend on the osmotic potential that controls the flow of water and salts between the inside and the outside of the cells. This is a life basis for organisms that make up the fauna and flora of the environment where the brine is disposed and/or injected.

This paper reviews the flow control mechanisms, and the dependence of osmotic potential on both the temperature and the composition of the brine, showing the variations that the osmotic potential naturally experiences in specific locations of desalination plants. As the environmental conditions of sea vary worldwide from a location to another one, the brine discharge conditions must be different for each location.

This paper aims to point out the necessity of defining more precisely the conditions of the disposal from RO plants through the osmotic potential concept, considering the brine temperature as a factor as important as the salinity of the same.

I. INTRODUCTION

To date a large number of reverse osmosis desalination plants, have set conditions of release based almost exclusively on the salinity maximum limits, but salinity by itself, regardless of the temperature does not affect the regulation of the flow between the flora and fauna and the environment.

The osmotic potential of the solution surrounding the cell regulates the flow of solutes and water between the inside and outside the cells.

Most discharge permits are based on the principle of environmental caution, given the lack of scientific information that supports the setting of limits for discharges above natural conditions. However some of these restrictions have forced to dilute the brine before being discharged into the sea, resulting in extra energy consumption and therefore CO_2 emissions.

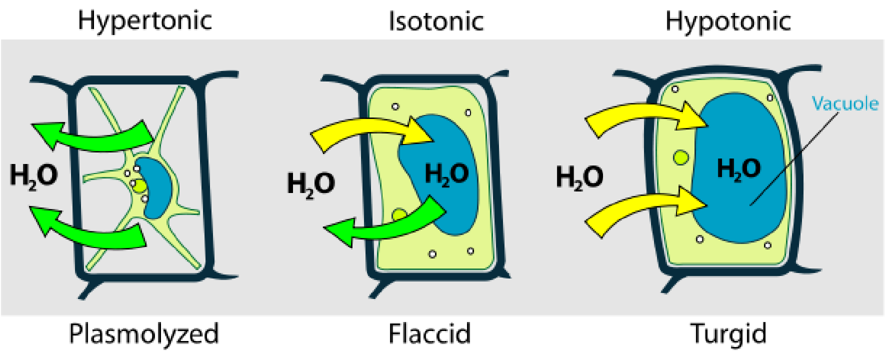
Throughout this article we try to demonstrate the importance of the osmotic potential in the discharge of desalination by RO so as to establish basic criteria to have into account when considering the environmental impact of the brine.

1.1 Physiology and water relations

Many people are not used to the concept of osmotic pressure, since it is not a pressure one can feel with the finger or measure with a simple gauge. And one of the reasons is because osmosis needs a semi-permeable membrane and for that reason the term osmotic potential is widely used. The osmotic potential is defined as the capability of a solution to suck water in if it was separated from another solution by a semi-permeable membrane. The highest water potential is 0, therefore the water potential is normally a negative number. So, the higher the negative number (the smaller the number, or the more negative) of the osmotic potential of a solution, the more it will suck water in, or the more concentrated it will be.

The terms isotonic, hypotonic and hypertonic describe the difference in osmotic pressure between two solutions with a certain osmotic potential. Two solutions are isotonic when the osmotic potentials are equal. When they are different, the one with the higher (read: less negative) potential will be hypotonic (less pressure) and the one with the lower potential (higher number or more negative) will be hypertonic (more pressure). (Fig.1)

Fig. 1



Osmosis is a phenomenon that takes place whenever there's a semi-permeable membrane. The cell membrane being one of such, makes osmosis one important phenomenon that must be taken into account by all living organisms. Plants use osmosis to increase turgor, and animal organisms need to control the osmotic pressure to avoid an over inflation and over shrinking of cells.

2.1 The water potential

The measure of the energy involved in osmosis is called water potential (ψ). Since the water must lose energy as it moves by osmosis, water must move from an area of greater potential to an area of less water potential:

- If the water potential is greater inside the cell than outside the cell, then there will be a net movement of water out of the cell.

- If the water potential is greater outside the cell than inside the cell, then osmosis will be a spontaneous net movement of water into the cell.

- If the water potential on each side of a cell membrane is the same, there is no net movement of water across the membrane.

This last condition is known as equilibrium. While individual molecules may migrate across the membrane at equilibrium, movements into the cell are balanced by movements out of the cell. Again, there is no net movement of water at equilibrium.

Three major parameters influence water potential: solute concentration or osmotic potential (ψ_s solute potential), hydrostatic pressure (ψ_p pressure potential) and gravity potential (ψg). They essentially have an additive effect:

$$\psi w = \psi s + \psi p + \psi g \qquad (1)$$

The presence of solutes dissolved in water lowers the water potential. Obviously then, water moves from an area where the solute concentration is lower to an area where the solute concentration is higher. Distilled water is the purest water (highest possible $\psi_s = 0$ MPa) and water with dissolved salts has lower water potential ($\psi_s < 0$, that is negative).

The exact solute potential (or *osmotic potential*) of a solution is determined by the van't Hoff equation as we'll see further in the text.

Water tends to move away from pressure. That is, pressure increases the water potential. At sea level, the pressure of the atmosphere is defined as 0 MPa. Negative pressures ($\psi_p < 0$) indicate that a partial vacuum (tension) is present; this is seldom observed in living plant tissues or cells, but may be common in dead cells of the xylem. When a vacuum is present, water will rush into it from an area of normal (0 MPa) pressure. Since a living plant cell has a cell wall, the movement of water into an already-filled cell can produce positive pressure ($\psi_p > 0$). This is frequently called turgor pressure. Since cells are normally completely filled with cytoplasm (cell volume ≥ 1.0), most adjustments needed to come to equilibrium with an external water potential influence pressure potential prior to significant changes in cell solute concentration.

Plant cells have a cell wall surrounding them. It is made of cellulose, a sugar polymer (the stuff paper is made of). This wall is quite rigid and it prevents the cell from bursting due to osmosis. The solution in the inner part of a plant cell is normally more concentrated than the outside. For that reason, if a plant cell has good access to water the cells will be stiffened and filled with water (due to osmosis), making the whole plant rigid. If the water is more concentrated (eg salty water) then the plant will lose rigidity and wilt.

Animal cells do not have the above mentioned cell wall. Many cells do have a so-called cytoskeleton, made out of proteins and small sugar chains in the inner part of the cell that are anchored to the cell membrane. In most cases this measure is enough to protect a cell from shrinking and bursting, but in a more narrow pressure range. For that reason many organisms are specialized to a certain environment, like fresh water or sweet water.

II. THE OSMOTIC POTENTIAL

2.1 Osmotic pressure

The first description of an experiment involving osmosis was given in 1748 by a man named Jean-Antoine Nollet (1700-1770), a French priest and scientist. But it wasn't until 1885, when a more accurate description of this phenomenon was given by a Dutch fellow by the name of Jacobus Henricus van't Hoff. He proposed that the dissolved particles in the solvent behave like ideal gas particles (see the Gas State Equations). According to this theory, the partial pressure (*p*) of these particles is given by the following equation. It was a modification of this simple equation that earned van't Hoff the chemistry Nobel prize in 1901:

$$p = (n/V)RT \qquad (2)$$

Where the quotient (n/V) is the amount of particles per volume, or the molar concentration (c), R is the gas constant (8.314 J·K-1·mol-1) and T the temperature (which is constant in this process). So, simplifying, the partial pressure is directly proportional to the concentration:

$$\psi s = - CiRT \qquad (3)$$

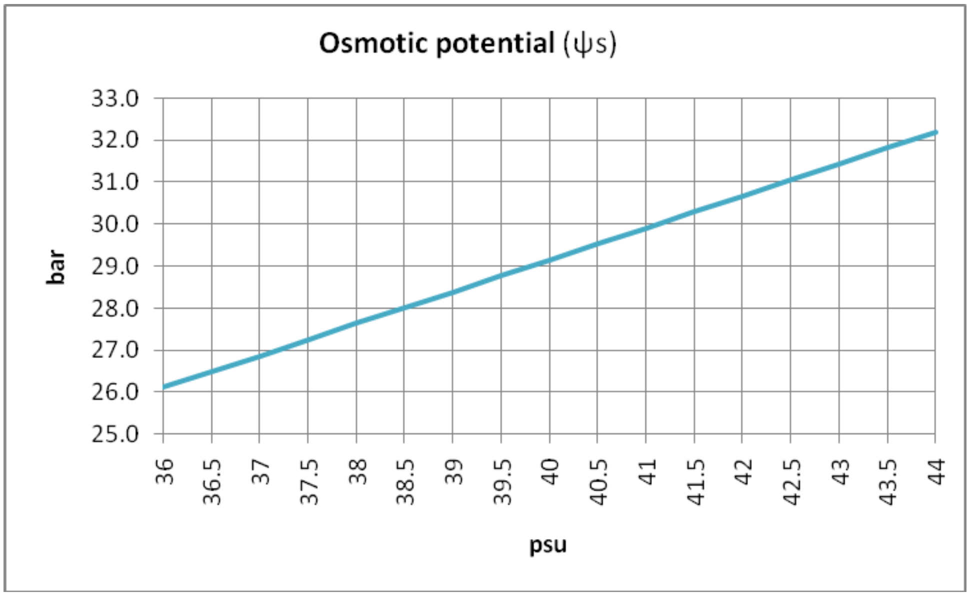
Here *C* is the molar concentration of the solutes, *i* is the osmotic coefficient, *R* is the gas constant, and *T* is the absolute temperature. The value of *i* is 1 for molecules that do not dissociate in solution and can be 2 or more for molecules that completely dissociate (such as salts). Recall that *C* is in units of moles liter^{-1}. The term *Ci* is the osmolar concentration or osmolarity of the solution. The osmolarity of a complex solution is the sum of the osmolarity of each of the solute components.

A pure water contains no solutes, thus, it should have zero (0) water potential. And also for this reason, the value of osmotic potential of a solution is always negative since the presence of solutes will always make a solution have less water than the same volume of pure water.

2.2 Influence of chemical composition

It's not the same the calculation of the osmotic potential based on the sum of molality of individual ions than the calculation through the conductivity of the solution. The value of the osmotic coefficient is 1 for molecules that do not dissociate in solution and can be 2 or more for molecules that completely dissociate (such as salts). Therefore is important the standardization of a calculation method for the osmotic potential, either from conductivity or for equivalent salinity in Na Cl as the membranes manufacturers use for the performance projections.

Fig. 2



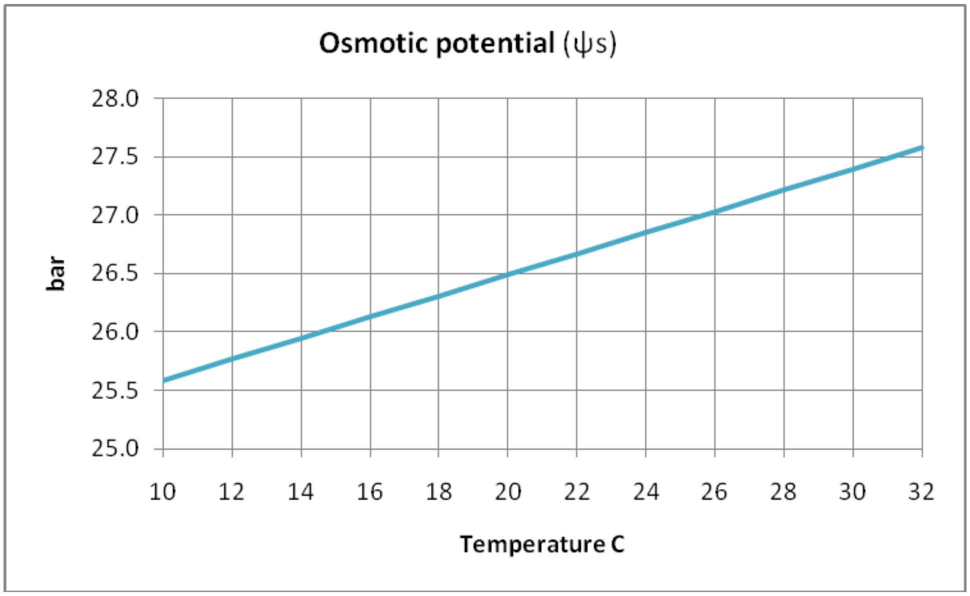
2.3 Temperature influence

As mentioned above, the osmotic potential is directly influenced by the temperature according the formula (3)

$$\Psi_s = - Ci\, R\, T,$$

For the same salinity, the temperature influence can suppose up to 2 bar difference between 10 and 32 degrees C.

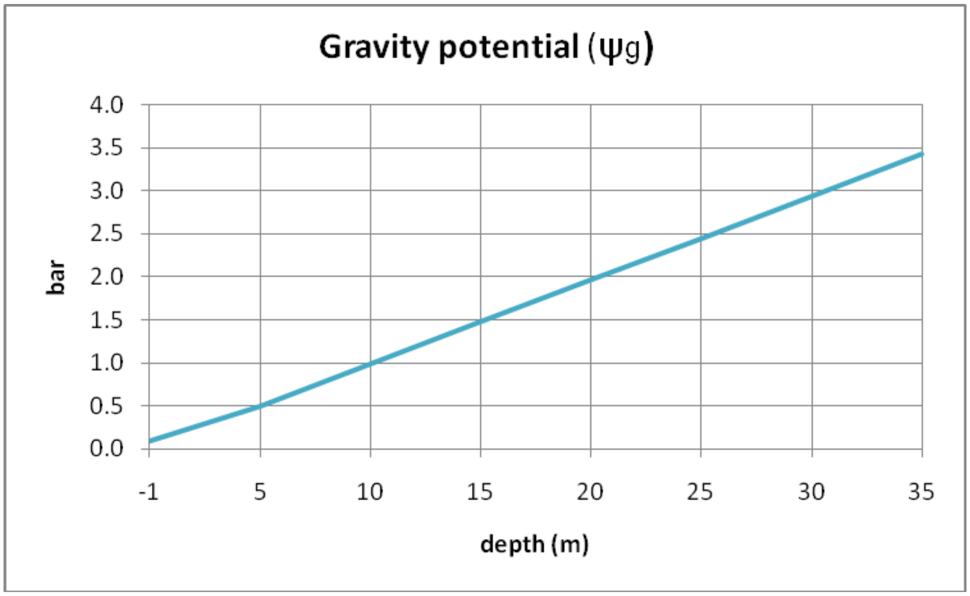
Fig. 3



2.4 Influence of depth

Gravity potential is usually ignored in shore calculations, but considering different bathymetrical scenarios, could have relative importance in case of marine environments, where *Posidonia oceanica*, i.e. can live between -2 and -30 m depth.

Fig. 4



2.5 Calculation procedure

One of the main problems when comparing results from different studies is the standardization of formulas used in the calculations, the measure units and the conditions under which these studies are carried out.

2.5.1 Practical Salinity

Practical salinity, *Sp* is defined on the Practical Salinity Scale of 1978 (Unesco (1981, 1983)) in terms of the conductivity ratio K15 which is the electrical conductivity of the sample at temperature t68 = 15 °C and pressure equal to one standard atmosphere (p = 0 dbar and absolute pressure P equal to 101 325 Pa), divided by the conductivity of a standard potassium chloride (KCl) solution at the same temperature and pressure. The mass fraction of KCl in the standard solution is 32.4356x10-3 (mass of KCl per mass of solution).

When K15 = 1, the Practical Salinity, *Sp* is by definition 35. Note that Practical Salinity is a unit-less quantity. Though sometimes convenient, it is technically incorrect to quote Practical Salinity in "psu"; rather it should be quoted as a certain Practical Salinity "on the Practical Salinity Scale PSS-78". When K15 is not unity, *Sp* and K15 are related by (Unesco, 1981, 1983) the PSS-78 equation:

$$S_P = \sum_{i=0}^{5} a_i \, (K_{15})^{i/2} \quad \text{where} \quad K_{15} = \frac{C(S_P, t_{68} = 15°\text{C}, 0)}{C(35, t_{68} = 15°\text{C}, 0)}, \tag{4}$$

i	a_i	b_i
0	0.0080	0.0005
1	- 0.1692	- 0.0056
2	25.3851	- 0.0066
3	14.0941	- 0.0375
4	- 7.0261	0.0636
5	2.7081	- 0.0144

For temperatures other than t_{68}=15 `C, Practical Salinity (*Sp*) is given by the following formula

$$S_P = \sum_{i=0}^{5} a_i \, (R_t)^{i/2} + \frac{(t_{68}/°\text{C} - 15)}{[1 + k(t_{68}/°\text{C} - 15)]} \sum_{i=0}^{5} b_i \, (R_t)^{i/2}.$$

Herewith is the comparison between the formulas for salinity calculations used in oceanography (Unesco PSS-78 and later revisions) and the formulas used in the normalization software of the main membrane manufacturers.

Sp (Unesco) = $1000*(6.859819E\text{-}38*C^{8}\ -2.027297E\text{-}32*C^{7} + 2.576767E\text{-}27*C^{6}\ -1.855032E\text{-}22*C^{5} + 8.450662E\text{-}18*C^{4}\ -0.00000000000002616744*C^{3} + 0.000000007096135*C^{2} + 0.0005161311*C - 0.05028803)$ (5)

Sp (Dow Norm.) = $0.0000000000801*\ e^{(((-50.6458\ -\ Ln(C))\ 2)\ /112.484}$ (6)

Sp (Toray Norm.) = $0.0000000000801*\ e^{(((-50.6458\ -\ Ln(C))\ 2)\ /112.484}$ (7)

Sp (Hydranautics) = $0.0662 * C$ (8)

where C is the seawater conductivity at 25 degrees and Sp salinity in psu

As is shown below, there are differences between the calculations made from different data and formulas, so this report is based on the selection of a method that is easily applicable to most desalination facilities.

Fig. 5

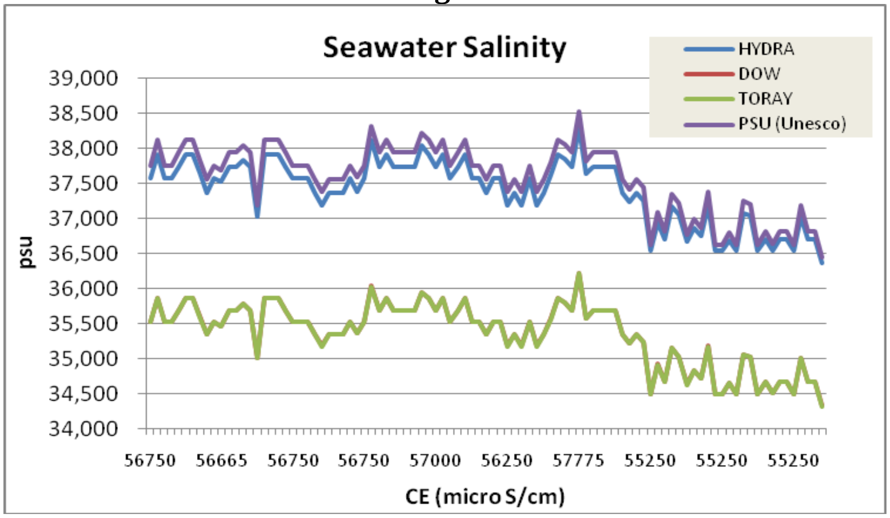
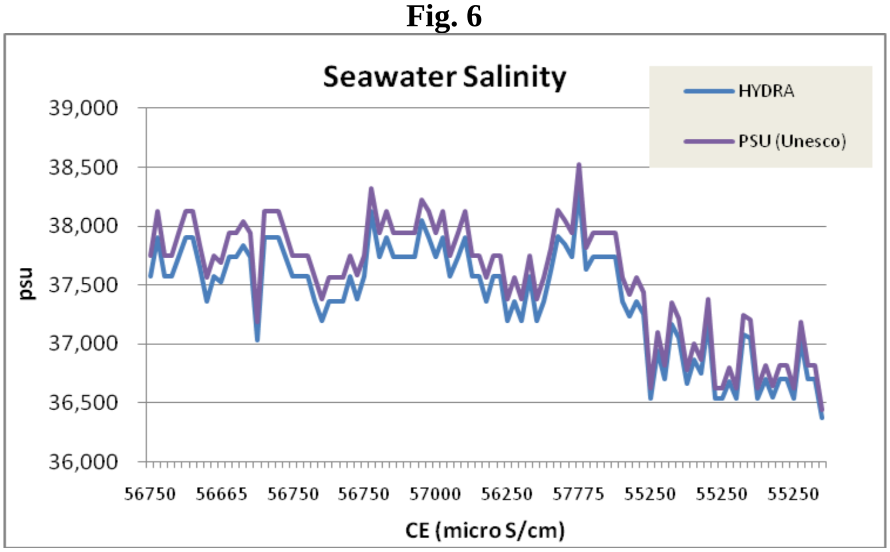


Fig. 6



If the sea water salinity is calculated using different formulas with the same conductivity, the osmotic pressure, will be different as well and therefore the results of the brine salinity that theoretical is disposed into the sea, what could modify the conclusions of the EIA of a proposed location for a desalination plant.

2.5.2. Osmotic pressure

As mentioned before, the osmotic pressure is calculated through the formula (1):

$$\pi o = \frac{n}{V} * R * T$$

However some deviations are found in the literature, especially in desalination publications and documents. The membranes manufacturers use the same formulas (9) (with small differences in decimals) in the normalization software to calculate de osmotic pressure, converting the conductivity into salinity and introducing this value in the formula instead of the sum of molalities of each ion.

$$\pi o = \frac{0.03851 * S * (T + 273{,}15)}{(1000 - (\frac{S}{1000})} * 14.5 \qquad (9)$$

Practically this approach makes easy the calculation of the osmotic pressure as the conductivity is the most common parameter used to check the seawater composition.
As the method to convert conductivity into salinity is different for each membrane manufacturer, this brings up different values of the osmotic pressure depending of the manufacturer for the same raw water quality.

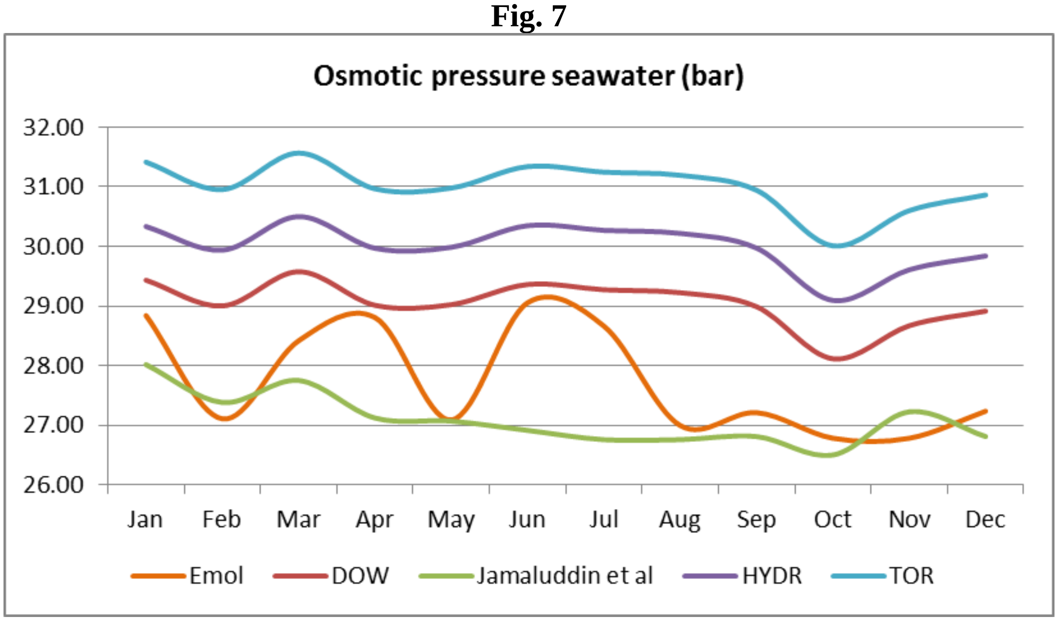
Some authors as Jamaluddin and others have proposed another formula to be used in the calculation of the osmotic pressure in the normalization process for RO membranes performance. In this method, the osmotic pressure is calculated directly from the seawater conductivity but as a result of a second order polynomial instead of a linear relationship between salinity and conductivity as used by Hydranautics (8).

$$\pi o = 0.038\, C^2 + 0.0944\, C + 9.8679 \qquad (10)$$

Next figure shows the differences between the osmotic pressure calculated from the same conductivity and temperature values, using the normalization software of each membrane manufacturers. In spite the membrane manufacturers use the same formula for the osmotic pressure, the uses of different formulas to convert conductivity into salinity result in different osmotic pressure values.

Note than in this paper the *psu* units for salinity and *bar* for pressure have been used instead of *mg/l* and *MPa* for better understanding due to their wide use in desalination industry.

Fig. 7



As is shown in the Fig.7 the osmotic pressure for the Mediterranean seawater of Valdelentisco plant changes from a minimum value of 26,5 bar, if calculated by Jamaluddin formula (10) up to a maximum value of 31,6 bar calculated by the formula used by Toray in its normalization software.

Such differences depending of the formula used for the calculation make difficult to compare results not only between different plant and locations, but also between membrane manufacturers. The paradox is that for the same plant, and operational parameters, the disposal of the Dow membranes would be less harmful than the brine from Toray, as the osmotic pressure and therefore the osmotic potential would be lower.

Therefore urges to set unique criteria to calculate the osmotic pressure from sea water temperature and conductivity, as both are the easiest parameters to be measured and are the widest used in desalination.

III. SITE EXAMPLES OF OSMOTIC POTENTIAL

2.1 Australia

Analysis carried out in Sidney show that seawater condition vary between 16,4 and 22,4 C for averages temperatures and between 29,04 and 33,53 psu for salinity.

Fig.8

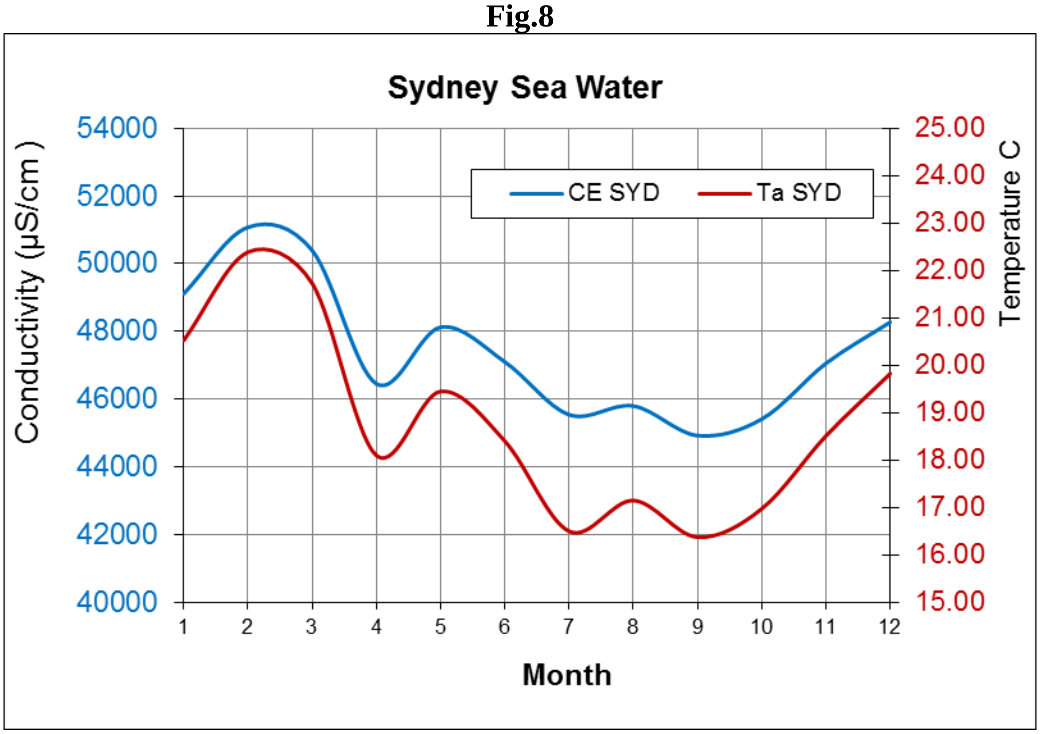
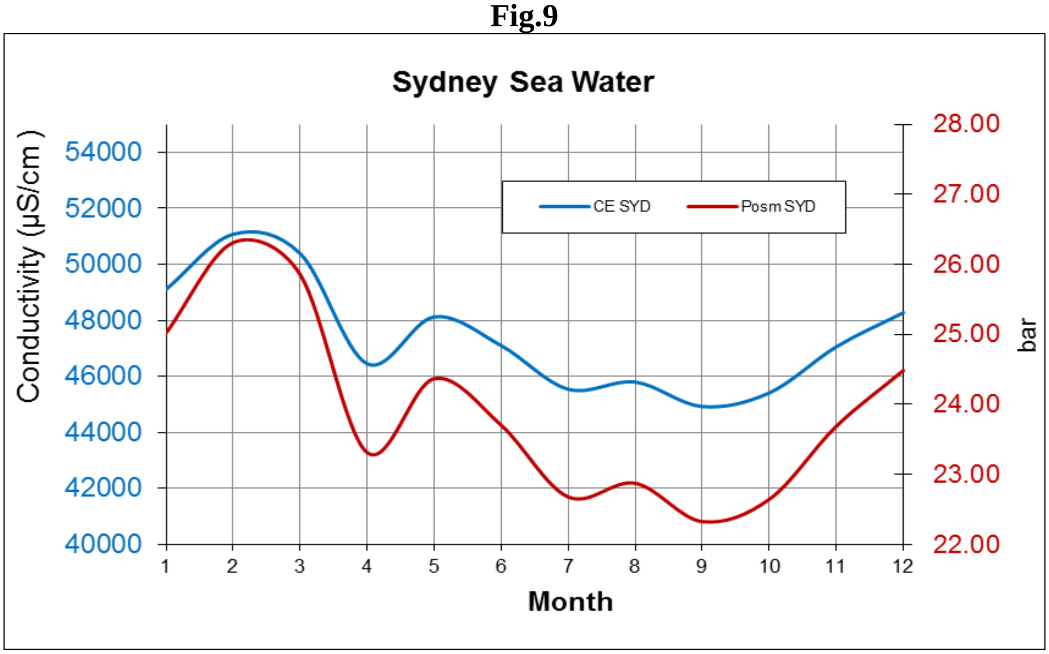


Fig.9



As a consequence of the calculation from seawater temperatures and conductivities, the osmotic pressure of the seawater changes between 22.3 bar and 26,3 bar.

In Australia, where *Posidonia australis* is present, some works as those carried out by Tyerman, S. D. and others, have shown that the specie is tolerant to changes in salinities within a range between 19 and 57 psu.

2.2 Mediterranean

Following figures show the annual variations in conductivity and temperature (Fig.10) and osmotic pressure for the seawater of Valdelentisco and Alicante desalination plants, separated 125 km away in the south east of Spain.

Fig.10

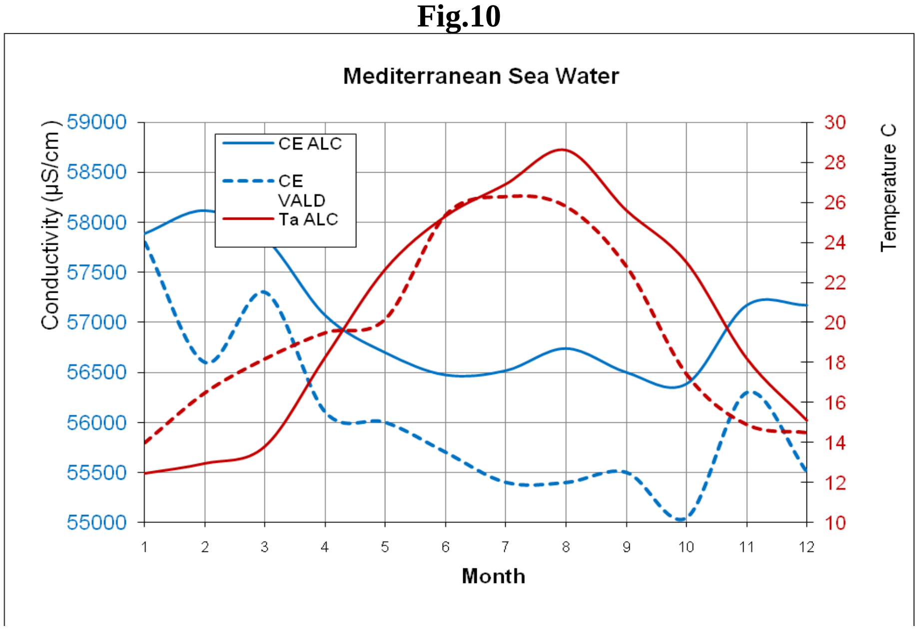
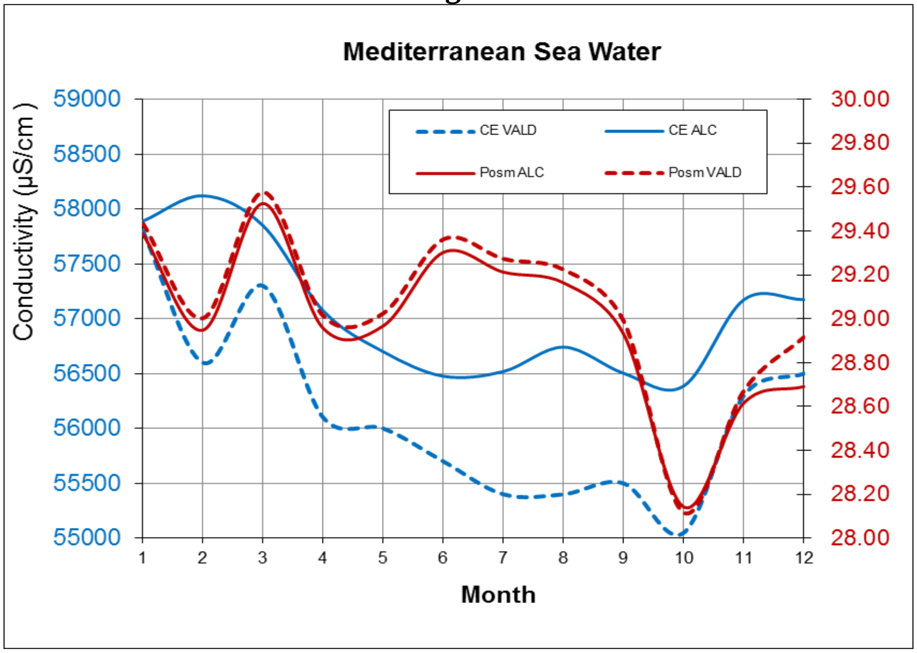


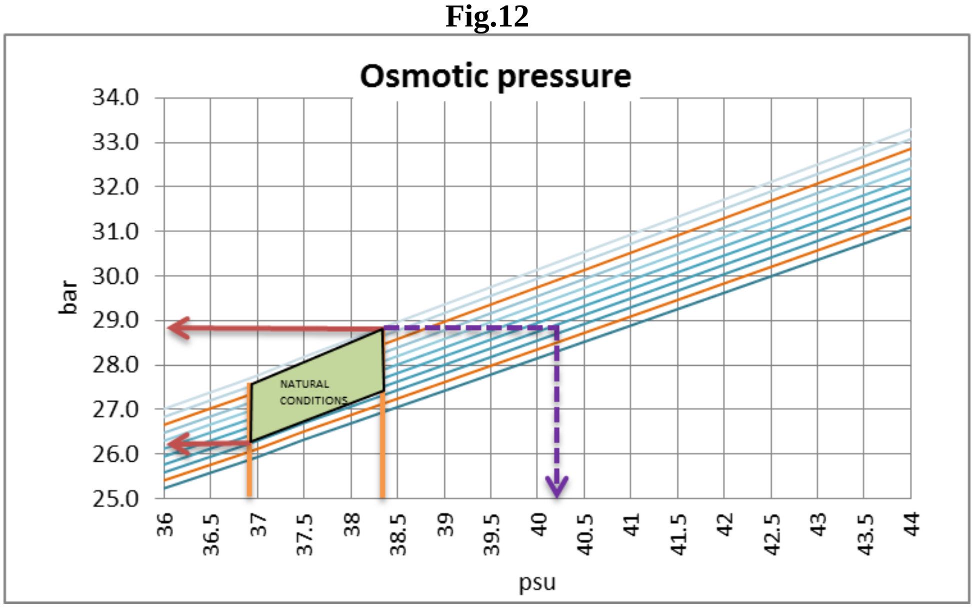
Fig.11



The osmotic pressure in these cases is highly influence for the temperature variations changing the tendency shown by the conductivity, especially during summer months when the temperatures are high. Above figure shows the calculated osmotic potential of the seawater from the summatory of the individual molalities of the ions as per formula 1.

This variation in the tendency of the osmotic pressure compare with the seawater conductivity, introduces the idea that there is a range of osmotic pressure for the seawater, in which marine flora and fauna live.

Fig.12



For the Valdelentisco plant location, a complete data analysis during one year showed the natural conditions of the seawater, with salinity (from conductivity) between 36,98 psu and 38,49 psu and temperature between 14,1 and 28,2 °C. Based on these natural limits, the osmotic interval fluctuates between 26,4 and 28,9 bars. Therefore the upper threshold where natural species (i.e. Posidonia oceanica) live is 28,9 bars at 28,2 °C, pressure that equals to 40,5 psu at 14 °C or 41 psu at 10 °C.

Therefore the osmotic pressure strongly depends on salinity and temperature as shown above and the dispossal thresholds must reflect the osmotic potential and not the salinity and temperature by separate. As a result, some species as i.e. Posidonia oceanica lives in an environment were ocasionally the salinity of the seawater could overcome the “natural value” of 38.49 psu.

Studies by biologists recommend that in those locations where there is seagrass, the brine discharge point must not exceed 38.5 psu, with no reference to the temperature of the receiving environment or brine. As we have seen, the flow of water in the plant depends on environmental conditions such as salinity and composition, temperature and depth. Some of the experiments were based on laboratory conditions with water from wells adding salts as ClNa to increase the salinity, resulting in a different osmotic potential that exists in the sea.

The impact of a brine of the same salinity is higher in summer than in winter due to the lower osmotic potential or higher osmotic pressure.

IV. CONCLUSIONS

- Osmotic pressure values changes for the same conductivity and temperature according the formula used for its calculation. It’s necessary to unify the criteria to calculate salinity and osmotic pressure of seawater and brine.

- The same osmotic potential can be obtained at different salinities and temperatures, therefore the osmotic pressure of the disposal must be the parameter to set the thresholds at the discharge location compared with the natural conditions of the marine environment instead of salinity and temperature independently.

- Discharge conditions for RO disposals should be conceptually agreed between all the members of the international desalination community (designers, operators, membrane manufacturers, environmentalists and authorities) and not to be exported from a facility location into another one.

- Thresholds values for RO disposals are different depending on plant location and environment conditions

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