

# How many ppm? The unresolved problem of acid dosing in the reverse osmosis plant design

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## Abstract

Different membrane manufacturer software are available for the designers of RO plants. Software releases are reissued periodically and distributed to the designers to make simulation of membrane behaviour. If you are familiar with these software you know that, a part the different products characteristics, depending on the membrane specification, the acid dosage requests to modify the pH of the feed water are very different for each supplier and often also for each software release. In the paper, using a data input a typical sea water Mediterranean Sea analysis, the membrane software are used to simulate different design conditions and the acid dosage figures are compared with those obtained from an original model developed by the authors, based on the carbonate salts equilibrium.

*Keywords:* Reverse osmosis; pH adjustment; Acid dosing; Sea water salinity; Carbonate system; Carbonic acid equilibrium

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## 1. Introduction

One of the main problem with that the reverse osmosis plant process engineer has to deal, when he has to design a new plant, is the chemical pre-treatment sizing.

In particular he has to define the pH of the feed to avoid the salts precipitation phenomenon and as consequence the acid flow rate to reach

the desired value of this parameter: in other words he has to define “how many ppm”

The scale control involves the carbonic species equilibrium calculation that is directly correlated to the pH trough the well known equilibrium reactions.

The software releases normally available by the membrane or chemical products manufacturer make the calculation starting from the feed pH value and the carbonates or bicarbonates content.

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In the following sections an overview of the different releases approaches is reported and compared with the classic equilibrium model to identify the correct acid dosing rate.

## 2. Software different approaches

Software of three membrane manufacturers is used for the comparison.

To compare the results the following standard analysis has been assumed as reference:

	Reference analysis
Sodium (ppm)	11,093
Potassium (ppm)	507
Calcium (ppm)	426
Magnesium (ppm)	1531
Bicarbonates (ppm)	188
Sulphates (ppm)	3698
Chlorides (ppm)	19,957
pH	8.1
Total dissolved solids (1) (ppm)	37,400

The following approaches are used by different manufacturers:

Manufacturer/chemical producer	Input	Parameter calculated
1	Sea water analysis Element age Bicarbonate content Carbonate content pH	CO <sub>2</sub> dissolved
2	Sea water analysis Fouling factor (year) Bicarbonate or carbonate content pH	Carbonate content or Bicarbonate content CO <sub>2</sub> dissolved
3	Sea water analysis Fouling factor (%) Bicarbonate or carbonate content pH	The pH is recalculated to match bicarbonate and carbonate content

### 2.1. Temperature influence

The reference acid used for pH adjustment is sulphuric acid at normalized concentration of 100% and the calculations have been made in the sea water temperature range 20–35°C.

In the following diagrams (Figs. 1–3) the acid dosing rate versus temperature to modify the feed pH from the raw water value of 8.1 to feed water value of 7.5 is reported for the different manufactures.

The curves for manufacturers number 2 and 3 have the same profile, but the manufacture 2 curve slope is greater than the slope of manufacturer 3 curve.

The dosing rate is decreasing with temperature increasing.

The manufacturer 1 dosing rate is from 2 to 2.2 times greater than the others and is increasing with temperature.

### 2.2. Final pH influence

The acid dosing rates vs. final pH starting from initial pH value of 8.1 are reported at two different temperatures 20 and 35°C in Figs. 4, 5 and 6.

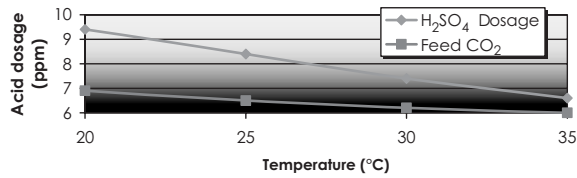


Fig. 1. H<sub>2</sub>SO<sub>4</sub> (100%) dosage vs. T(°C) pH 8.1–7.5—manufacturer 1.

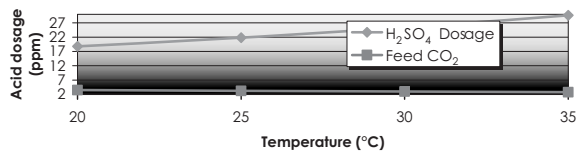


Fig. 2. H<sub>2</sub>SO<sub>4</sub> (100%) dosage vs. T(°C) pH 8.1–7.5—manufacturer 2.

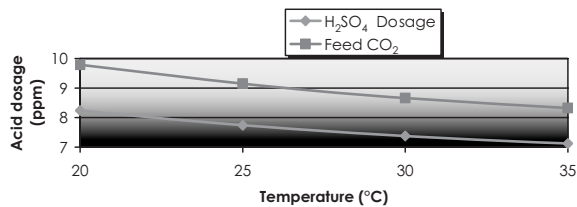


Fig. 3. H<sub>2</sub>SO<sub>4</sub> (100%) dosage vs. T(°C) pH 8.1–7.5—manufacturer 3.

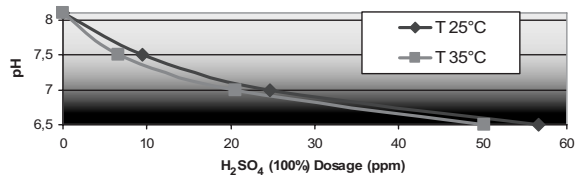


Fig. 4. H<sub>2</sub>SO<sub>4</sub> (100%) dosage vs. final pH—manufacturer 1.

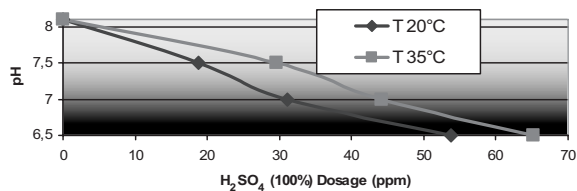


Fig. 5. H<sub>2</sub>SO<sub>4</sub> (100%) dosage vs. final pH—manufacturer 2.

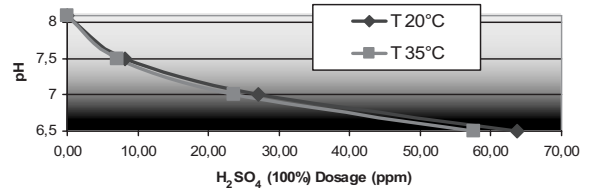


Fig. 6. H<sub>2</sub>SO<sub>4</sub> (100%) dosage vs. final pH—manufacturer 3.

*Manufacturer 1:* The dosing rate is increasing whereas the final pH is decreasing; the curve is concave; the dosing rate is higher for lower temperatures.

*Manufacturer 2:* The dosing rate is increasing whereas the final pH is decreasing; the curve is convex; the dosing rate is higher for higher temperatures.

*Manufacturer 3:* The dosing rate is increasing whereas the final pH is decreasing; the curve is concave; the dosing rate is higher for lower temperatures.

The behaviour is similar to the Manufacturer 1.

### 3. Carbonic acid equilibrium

The pH of most natural waters included the sea water is generally assumed to be controlled by the carbonic acid system [1,2,5,6].

The applicable equilibrium reactions are:



The CO<sub>2</sub>/HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> equilibrium in sea water can be calculated starting from Alkalinity and pH values through the calculation of the following equations:

$$K_w = [\text{H}^+] \cdot [\text{OH}^-]$$

$$K_1 = \frac{[\text{H}^+] \cdot [\text{HCO}_3^-]}{[\text{CO}_2]}$$

$$K_2 = \frac{[\text{H}^+] \cdot [\text{CO}_3^{=}]}{[\text{HCO}_3^-]}$$

where:

$$K_w = \text{ionisation product of water} \\ = 10^{6.0486 - \frac{4471.33}{T_w + 273} - 0.017053 \cdot (T_w + 273)}$$

$$K_1 = \text{first dissociation constant} \\ = 10^{14.8435 - \frac{3404.71}{T_w + 273} - 0.032786 \cdot (T_w + 273)}$$

$$K_2 = \text{second dissociation constant} \\ = 10^{6.498 - \frac{2909.39}{T_w + 273} - 0.02379 \cdot (T_w + 273)}$$

The following relations have to be taken into account:

$$[\text{Alk}] = \frac{\text{total alkalinity as CaCO}_3 \cdot \text{gr - equiv}}{50 \times 1000} \cdot \frac{1}{1}$$

$$[\text{H}^+] = \text{hydrogen ions concentration} \cdot \frac{\text{gr - ions}}{1} \\ = 10^{-\text{pH}}$$

$$[\text{HCO}_3^-] = \frac{\text{ppm} \cdot [\text{HCO}_3^-]}{61 \times 1000} \cdot \frac{\text{gr - ions}}{1}$$

$$[\text{CO}_3^{=}] = \frac{\text{ppm} \cdot [\text{CO}_3^{=}]}{60 \times 1000} \cdot \frac{\text{gr - ions}}{1}$$

$$[\text{CO}_2] = \frac{\text{ppm} \cdot [\text{CO}_2]}{44 \times 1000} \cdot \frac{\text{gr - ions}}{1}$$

The following ionic balance can be also written:

$$[\text{Alk}] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{=}] + [\text{OH}^-]$$

And using the ionisation and dissociation constants defined above, the following final relations are obtained:

$$[\text{HCO}_3^-] = \frac{[\text{Alk}] + [\text{H}^+] - \frac{K_w}{[\text{H}^+]}}{1 + \frac{2K_2}{[\text{H}^+]}} \cdot \frac{\text{gr - ions}}{1}$$

$$[\text{CO}_3^{=}] = \frac{K_2}{[\text{H}^+]} \cdot [\text{HCO}_3^-] \cdot \frac{\text{gr - ions}}{1}$$

$$[\text{CO}_2] = \frac{[\text{H}^+]}{K_1} \cdot [\text{HCO}_3^-] \cdot \text{gr - moles}$$

For a defined pH and alkalinity or carbonate content is possible to determine the bicarbonate content that contribute to the CO<sub>2</sub> formation.

In conclusion is clear that the parameters carbonates, bicarbonates, CO<sub>2</sub> and pH are correlated and, if three parameters are defined, the fourth is consequently determined.

The acid addition can be defined according to the previous defined equations.

#### 4. Calculation model

The model developed has been already described in the previous work of same authors [7,3,4]. In particular for each stream the following parameters are calculated:

- ionic salt balance
- carbonic species equilibrium pH
- saturation pH

In the case that an energy recovery device is used the raw water analysis input is corrected taking into account the PX salt losses to make the exact feeding conditions at the membranes inlet:

The chemicals dosing rate for the feed water are calculated starting from the raw water analysis and for each step of the treatment the complete carbonic species equilibrium is calculated.

The main feature of the new calculation system is that the water quality in terms of pH, TDS and carbonic species during the various phases of the process can be followed

and the PX effect on the system performances is taken into account, carrying out a new approach to the RO plant design software.

**5. Calculation model results**

In the following Figs. 7 and 8 the original model calculation results are reported compared

with the manufacturers models; as usual “in medio stat virtus”.

In other words the theoretical model in a good agreement with the manufactures 1 and 3, whereas the manufacturer no. 2 that is completely out of the normal figures.

The consequence is that the acid consumption is not corrected; this fact implies

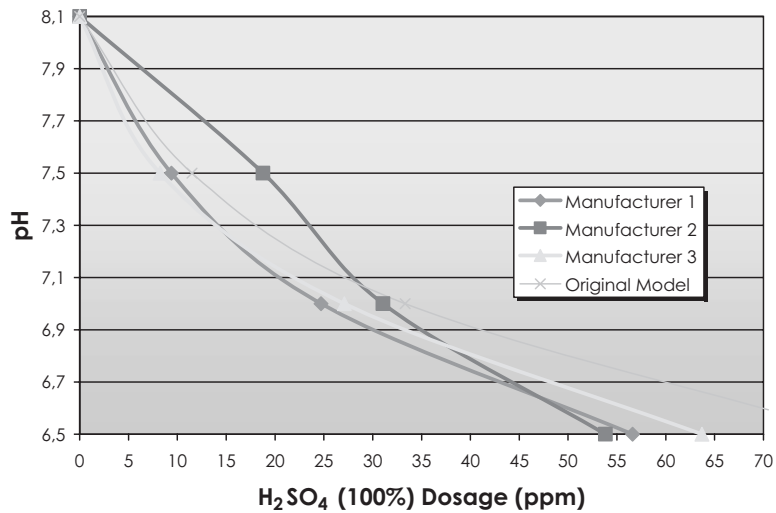


Fig. 7. H<sub>2</sub>SO<sub>4</sub> (100%) dosage vs. final pH—T 20°C.

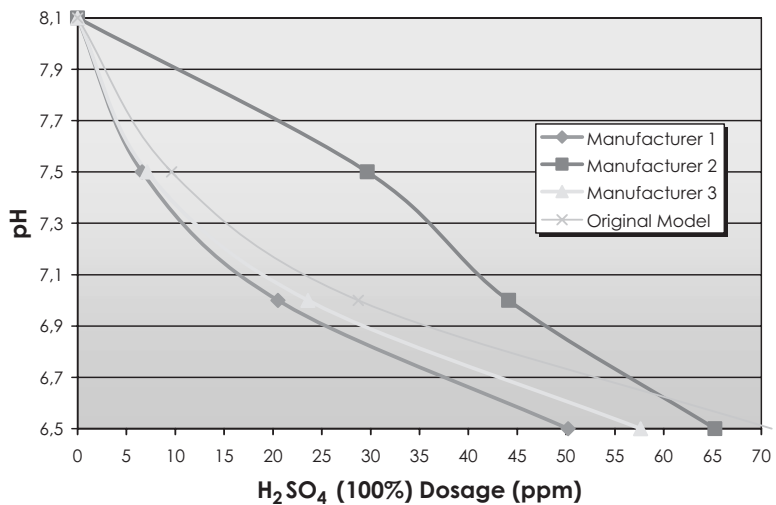


Fig. 8. H<sub>2</sub>SO<sub>4</sub> (100%) dosage vs. final pH—T 35°C.

that the chemical dosing section is oversized with a consequent plant extra cost.

Moreover the water production cost can be estimated more than the real one.

**6. What is the true?**

In the last Figs. 9, 10 and 11 the classical representation of carbonic acid equilibrium are shown for different manufacturers and for the

authors. The manufacturer 1 curve profile is in good agreement with the theoretical model, whereas the manufacturer 2 curve presents some differences.

In particular for Manufacturer 2 carbonate species are present for pH around 8.

The consequence of the use of a not correct model is already evidenced in the previous figures, because the acid dosage estimation is greater than the necessary.

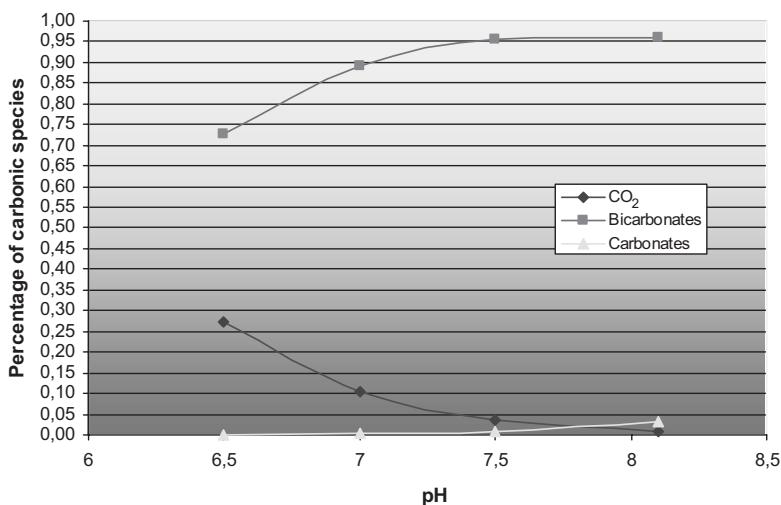


Fig. 9. Carbonic species equilibrium at 20°C—manufacturer 1.

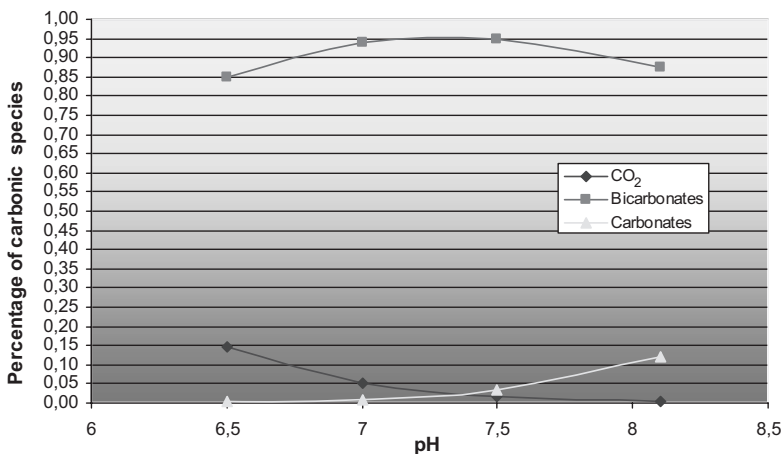


Fig. 10. Carbonic species equilibrium at 20°C—manufacturer 2.

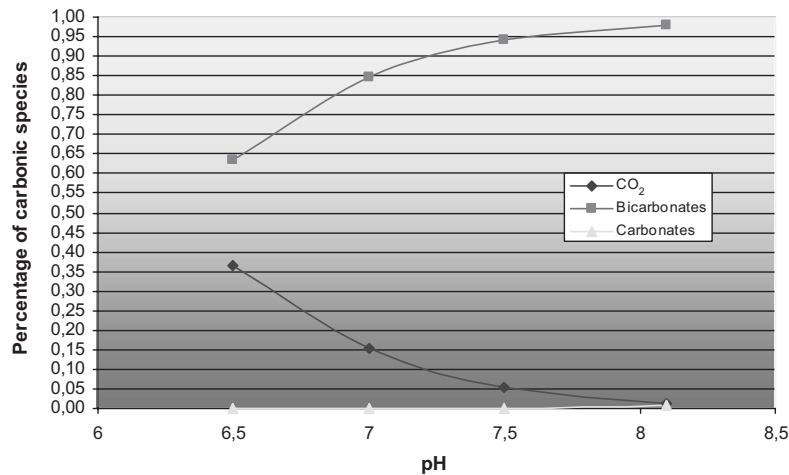


Fig. 11. Carbonic species equilibrium at 20°C: theoretical model.

## 7. Conclusions

The software produced by manufacturers can be used with particular attention; the theory can not be missed and the feed back of the membrane suppliers have to disclaim to the engineering companies to allow the best design of RO plants to avoid over sizing of chemical pre-treatment sections with unnecessary extra cost.

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