

# VALIDATION OF A METHOD FOR MODELING BRINE AND PERMEATE pH IN RO AND NF SYSTEMS

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## **ABSTRACT**

Concentrate pH in RO and NF applications plays a significant role in the formation of certain scales and the rejection of various contaminants. Incorrectly predicting pH can lead to excessive chemical costs or operational issues. Likewise, permeate pH is of utmost importance for determining post-treatment requirements for the product water.

Most membrane and antiscalant projection software currently use a method similar to that of the ASTM standard D3739 for predicting concentrate and permeate pH. These calculations assume that the concentration of carbon dioxide in the feed, permeate and concentrate are equivalent. They determine the pH in each stream based on the equilibrium relationship according to the ratio of bicarbonate to carbon dioxide concentrations.

When comparing calculated values to measured pH values in real systems, it becomes very apparent that methods relying on HCO<sub>3</sub>/CO<sub>2</sub> ratio predict concentrate and permeate pH very poorly outside a feed pH range of 5 - 6. They are overly conservative, always predicting excessively high concentrate pH values and excessively low permeate pH values. In real-world applications, there are cases where the measured concentrate pH is lower than the feed pH or where the permeate pH is higher. Such cases are never predicted correctly using the HCO<sub>3</sub>/CO<sub>2</sub> ratio, which always determines that the concentrate pH must be higher than the feed pH, and that the permeate pH must be lower than the feed pH. Some have recently attempted to correct for this phenomenon by using the equilibrium relationship of carbonate to bicarbonate at higher feed pH, but we have found such calculated values to be inconsistent and unreliable. Others have looked at the interaction of hydronium and hydroxide ions with the membrane, but in the presence of any weak acids, the pH would only be impacted by free hydronium or hydroxide ion concentrations at pH extremes.

The approach described in this paper predicts concentrate and permeate pH very reliably in RO and NF systems. This model has been tested against real systems and verified to predict concentrate and permeate pH very accurately across the entire pH range. It has been found to be accurate in brackish water, seawater and industrial reuse applications.

This paper describes how the pH calculation method was derived and provides examples where the model was compared to onsite measurements for various types of feedwater.

**Keywords:** *RO Brine pH, RO Concentrate pH, RO Permeate pH, Reverse Osmosis, pH Prediction Calculation*



## I. INTRODUCTION

A reliable method for predicting concentrate and permeate pH values is essential for accurately predicting operation and maintenance (O&M) costs in nanofiltration (NF) and reverse osmosis (RO) systems. An overly high concentrate pH in a projection will lead to an excessive calcium carbonate scaling prediction, prompting the need for excessive pH reduction where none may be needed, and higher antiscalant dosages than necessary.

The most commonly used pH prediction model in the membrane industry depends on the equilibrium relationship between bicarbonate and carbonic acid. However, the concentrate and permeate pH values measured at membrane plants are significantly different than those predicted by the  $\text{HCO}_3^-/\text{CO}_2$  model. In fact, it was found that the  $\text{HCO}_3^-/\text{CO}_2$  model only gave realistic concentrate and permeate pH values in the pH range of 5 – 6.

## II. BACKGROUND

The most commonly used concentrate pH prediction model assumes that carbonic acid is not rejected by RO membranes, and is therefore equal in the feed, permeate and concentrate. The bicarbonate concentration in the brine is calculated as a function of recovery and salt rejection, where:

$$\text{Concentration Factor} = [1 - (\text{Recovery})(\text{Salt Passage})]/(1 - \text{Recovery}) \quad (1)$$

And the pH is calculated from the following relationship:

$$K_{a1} = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] \quad (2)$$

Where;

$K_{a1}$  is the first dissociation constant for carbonic acid and is a function of temperature.  
 $[\text{H}_2\text{CO}_3]$  is assumed to be equal to  $[\text{CO}_2]$

Although the  $\text{HCO}_3^-/\text{CO}_2$  model does not stipulate this, ionic activities must be considered to account for ionic strength:

$$\alpha_{\text{H}^+} = K_{a1} \cdot \alpha_{\text{H}_2\text{CO}_3} / \alpha_{\text{HCO}_3^-} \quad (3)$$

$$\text{pH} = -\log (\alpha_{\text{H}^+}) \quad (4)$$

Using such a method yields a dilemma. The equilibrium relationship is being violated when the  $\text{CO}_2$  concentration is assumed to be constant. As alkalinity is rejected, the  $\text{CO}_2$  concentration must increase to maintain equilibrium. Most membrane projection software recalculate the inorganic carbon species in the brine at the predicted pH.

When calculating the total charges for cations and anions, this is highly problematic at feed pH > ~8.3, since the brine pH is always higher than the feed pH using this method. The formation of divalent carbonate ions means that electroneutrality cannot be attained. If we attempt to maintain electroneutrality on the feed/concentrate side by increasing the rejection of cations, the charges on the permeate side will be highly unbalanced.



By comparison, when measured brine and permeate pH values are used in calculating the total charges, it is noted that electroneutrality is always achieved.

Nir et al attempted to develop an improved permeate pH prediction by modelling the transport of hydronium and hydroxide ions through the membrane[1]. However, without accounting for weak acids, such a model would only be valid at pH extremes or in unbuffered water.

Waly et al suggested that the  $\text{HCO}_3/\text{CO}_2$  equilibrium model is unreliable when feed water pH is high because the  $\text{CO}_2$  concentration is too low for the first dissociation constant to be relevant [2]. As part of their study, they evaluated the PHREEQC evaporation model which accounts for ion complexation. However, they found a better fit to their measured pH values when using the  $\text{CO}_3/\text{HCO}_3$  equilibrium. They hypothesized that the second dissociation constant would dominate at higher feed pH conditions and provide a more reliable method for predicting brine pH:

$$K_{a2} = \alpha\text{CO}_3^{2-} \cdot \alpha\text{H}^+ / \alpha\text{HCO}_3^- \quad (5)$$

$$\alpha\text{H}^+ = K_{a2} \cdot \alpha\text{HCO}_3^- / \alpha\text{CO}_3^{2-} \quad (6)$$

In testing this model, we found that such an approach only works in a very narrow pH window for an extremely specific water quality. A concentrate or permeate pH prediction model should be effective for any water quality and valid for the entire feed pH range.

The use of the  $\text{HCO}_3/\text{CO}_2$  equilibrium relationship is often justified by the fact that carbonic acid is the dominant weak acid in most natural waters and should therefore have the biggest influence on pH. While this assumption is true, it is also exactly the reason that using that assumption yields only a loose estimate of the concentrate and permeate pH and becomes completely irrelevant at higher feed pH. Such an assumption also becomes irrelevant in industrial process waters which may contain other weak acids as the predominant buffers, or mining waters with feed pH values too low for any bicarbonate to exist.

Applying a model that accounts for ion complexation while also considering for ion rejection of the various species will result in an exceptionally reliable pH prediction for both permeate and concentrate pH.

Nir and Oded [3] coupled solution-diffusion and film layer models to PHREEQC so that all weak acids and ion pairs would be considered in determining brine pH in seawater RO. Although this approach is conceptually similar to that described in this paper, the model requires the use of four different software, and we were unsuccessful in our attempts to run it to compare against our own model.

### III. THEORY

Passage of ions through the membrane will vary depending on charge, charge density [4], molecular weight and molecular structure. While most pH models only consider for bicarbonate and carbon dioxide, all weak acid and weak base species in the concentrate and permeate streams will impact the respective pH values. The concentrations of these species are in turn impacted by formation of ion complexes.

In all cases where the concentrate or permeate pH calculated using the HCO<sub>3</sub>/CO<sub>2</sub> equilibrium differed significantly from actual values measured at a plant, the anion and cation charges were unbalanced. Therefore, in attempting to model pH for such cases, we focused on electroneutrality.

*Table 1: Ion complexes formed in solution consisting of calcium, sodium, sulfate, chloride and carbonate alkalinity.*

Chemical Equation	Equilibrium Equation
$H_2CO_3 = HCO_3^- + H^+$	$K_{a1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$
$HCO_3^- = CO_3^{2-} + H^+$	$K_{a2} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$
$Na^+ + HCO_3^- = NaHCO_3^0$	$K_{eq} = \frac{[NaHCO_3^0]}{[Na^+][HCO_3^-]}$
$Na^+ + CO_3^{2-} = NaCO_3^-$	$K_{eq} = \frac{[NaCO_3^-]}{[Na^+][CO_3^{2-}]}$
$Ca^{2+} + HCO_3^- = CaHCO_3^+$	$K_{eq} = \frac{[CaHCO_3^+]}{[Ca^{2+}][HCO_3^-]}$
$Ca^{2+} + CO_3^{2-} = CaCO_3^0$	$K_{eq} = \frac{[CaCO_3^0]}{[Ca^{2+}][CO_3^{2-}]}$
$HSO_4^- + H^+ = SO_4^{2-}$	$K_{a2} = \frac{[SO_4^{2-}]}{[HSO_4^-][H^+]}$
$Na^+ + SO_4^{2-} = NaSO_4^-$	$K_{eq} = \frac{[NaSO_4^-]}{[Na^+][SO_4^{2-}]}$
$Ca^{2+} + SO_4^{2-} = CaSO_4^0$	$K_{eq} = \frac{[CaSO_4^0]}{[Ca^{2+}][SO_4^{2-}]}$
$Ca^{2+} + Cl^- = CaCl^+$	$K_{eq} = \frac{[CaCl^+]}{[Ca^{2+}][Cl^-]}$
$Ca^{2+} + H_2O = CaOH^+ + H^+$	$K_{eq} = \frac{[CaOH^+][H^+]}{[Ca^{2+}]}$
$Na^+ + H_2O = NaOH^0 + H^+$	$K_{eq} = \frac{[NaOH^0][H^+]}{[Na^+]}$
$H^+ + OH^- = H_2O$	$K_w = [H^+][OH^-]$

In a relatively simple solution, consisting of calcium, sodium, sulfate, chloride and carbonate alkalinity, multiple ion complexes will form (Table 1). By accounting for these ion complexes for each species:

- (I) Total Ca =  $[Ca^{2+}] + [CaCl^+] + [CaHCO_3^+] + [CaCO_3^0] + [CaSO_4^0] + [CaOH^+]$
- (II) Total Na =  $[Na^+] + [NaHCO_3^0] + [NaCO_3^-] + [NaSO_4^-] + [NaOH^0]$
- (III) Total C =  $[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + [NaHCO_3^0] + [NaCO_3^-] + [CaHCO_3^+] + [CaCO_3^0]$
- (IV) Total SO<sub>4</sub> =  $[HSO_4^-] + [SO_4^{2-}] + [NaSO_4^-] + [CaSO_4^0]$
- (V) Total Cl =  $[Cl^-] + [CaCl^+]$

And accounting for electroneutrality:

$$(VI) [Ca^{2+}] + [CaCl^+] + [CaHCO_3^+] + [CaOH^+] + [Na^+] + [H^+] = [HSO_4^-] + [SO_4^{2-}] + [HCO_3^-] + [CO_3^{2-}] + [NaCO_3^-] + [NaSO_4^-] + [Cl^-] + [OH^-]$$

And then substituting:

- (i) Total Ca =  $[Ca^{2+}] \{1 + [Cl^-]/K_{eqCaCl} + [HCO_3^-]/K_{eqCaHCO_3} + [HCO_3^-]K_{aCO_3}/([H^+]K_{eqCaCO_3}) + [SO_4^{2-}]/K_{eqCaSO_4} + K_{eqCaOH}/[H^+]\}$
- (ii) Total Na =  $[Na^+] \{1 + [HCO_3^-]/K_{eqNaHCO_3} + [HCO_3^-]K_{aCO_3}/([H^+]K_{eqNaCO_3}) + [SO_4^{2-}]/K_{eqNaSO_4} + K_{eqNaOH}/[H^+]\}$
- (iii) Total C =  $[HCO_3^-] \{1 + [H^+]/K_{aHCO_3} + K_{aCO_3}/[H^+] + [Na^+]/K_{eqNaHCO_3} + [Na^+]K_{aCO_3}/([H^+]K_{eqNaCO_3}) + [Ca^{2+}]/K_{eqCaHCO_3} + [Ca^{2+}]K_{aCO_3}/([H^+]K_{eqCaCO_3})\}$
- (iv) Total SO4 =  $[SO_4^{2-}] \{1 + [H^+]/K_{aHSO_4} + [Na^+]/K_{eqNaSO_4} + [Ca^{2+}]/K_{eqCaSO_4}\}$
- (v) Total Cl =  $[Cl^-] \{1 + [Ca^{2+}]/K_{eqCaCl}\}$
- (vi)  $[Ca^{2+}] + [Ca^{2+}][Cl^-]/K_{eqCaCl} + [Ca^{2+}][HCO_3^-]/K_{eqCaHCO_3} + [Ca^{2+}]K_{eqCaOH}/[H^+] + [Na^+] + [H^+] = [HSO_4^-] + [SO_4^{2-}] + [HCO_3^-] + [CO_3^{2-}] + [Na^+][HCO_3^-]K_{aCO_3}/([H^+]K_{eqNaCO_3}) + [Na^+][SO_4^{2-}]/K_{eqNaSO_4} + [Cl^-] + K_w/[H^+]$

Six equations and six unknown variables are obtained. The equilibrium constants will all be impacted by temperature and ionic activity (as a function of ionic strength).

In solving these equations, the hydronium ion concentration is obtained, allowing for calculation of the pH according to the following relationship:

$$pH = -\log \alpha_{H^+} = -\log (Y_{H^+}[H^+]) \quad (7)$$

In most cases, there are many more parameters to consider, and the calculations can be significantly more complex. However, the same principle can be applied to any water quality and will always result in accurate concentrate and permeate pH calculations, so long as membrane rejection of the various ions are considered.

#### IV. VALIDATION

This method was validated at various water plants, using different membrane types, configurations and recoveries.

**\* The ASTM method calculates concentrate pH for the purposes of LSI calculation, but does not involve calculation of the permeate pH.**



Example 1:

Seawater RO (Internally Staged LG SW440 R X 5 → LG SW400 R X 2)  
 Recovery: 51%, Feedwater Temp: 15.5 °C

	Feed pH	Concentrate pH	Permeate pH
ASTM* Method	7.61	7.9	-
Membrane Manufacturer Projection		8.05	5.48
AWC Proton® Projection		7.50	5.97
Actual		7.47	5.88

Example 2:

Brackish Water RO (Hybrid System 1<sup>st</sup> Stage Filmtec BW30LE-440 → 2<sup>nd</sup> Stage Filmtec XLE-440)  
 Recovery: 75%, Feedwater Temp: 23.6 °C

	Feed pH	Concentrate pH	Permeate pH
ASTM* Method	7.41	8.0	-
Membrane Manufacturer Projection		7.5	6.40
AWC Proton® Projection		7.55	6.52
Actual		7.58	6.61

Example 3:

High TDS Brackish Water RO  
 (Hybrid System 1<sup>st</sup> Stage Filmtec SW30XLE-400 → 2<sup>nd</sup> Stage Filmtec SW30ULE-400)  
 Recovery: 71%, Feedwater Temp: 25.6 °C

	Feed pH	Concentrate pH	Permeate pH
ASTM* Method	6.53	7.2	-
Membrane Manufacturer Projection		6.9	5.00
AWC Proton® Projection		6.77	5.17
Actual		6.82	5.34



Example 4:

Brackish RO (2 stage Toray TMH20A-400C)  
 Recovery: 83%, Feedwater Temp: 21.6 °C

	Feed pH	Concentrate pH	Permeate pH
ASTM* Method	7.09	7.9	-
Membrane Manufacturer Projection		7.74	5.63
AWC Proton® Projection		7.48	6.07
Actual		7.50	5.76

Example 5:

Brackish RO (2 stage Hydranautics ESPA2-LD)  
 Recovery: 75%, Feedwater Temp 27.5 °C

	Feed pH	Concentrate pH	Permeate pH
ASTM* Method	7.43	8.0	-
Membrane Manufacturer Projection		7.94	6.52
AWC Proton® Projection		7.62	6.18
Actual		7.65	6.06

Example 6:

Brackish NF (Internally Staged: 1st Stage Filmtec NF90, 2nd Stage NF90 X 3 → NF270 X 4)  
 Recovery: 84.1%, Feedwater Temp 25.1 °C

	Feed pH	Concentrate pH	Permeate pH
ASTM* Method	6.25	6.9	-
Membrane Manufacturer Projection		6.8	5.8
AWC Proton® Projection		6.74	6.00
Actual		6.76	6.02



Example 7:

2nd Pass SWRO (Hybrid System:

1st & 2nd Stage Filmtec BW30-400/34 → 3rd & 4th Stage LG SW 440 SR )

Recovery: 95%, Feedwater Temp 28.5 °C

	Feed pH	Concentrate pH	Permeate pH	
ASTM* Method	10.08	-	-	
Membrane Manufacturer Projection (WAVE 1 <sup>st</sup> & 2 <sup>nd</sup> Stage)		10.7	1 <sup>st</sup> Stage	8.3
			2 <sup>nd</sup> Stage	8.7
Membrane Manufacturer Projection (LG 3 <sup>rd</sup> & 4 <sup>th</sup> Stage)		11.10	3 <sup>rd</sup> Stage	8.25
			4 <sup>th</sup> Stage	8.68
AWC Proton <sup>®</sup> Projection		10.59	1 <sup>st</sup> Stage	9.51
			2 <sup>nd</sup> Stage	9.60
			3 <sup>rd</sup> Stage	10.11
			4 <sup>th</sup> Stage	10.16
Actual		10.55	1 <sup>st</sup> Stage	9.62
			2 <sup>nd</sup> Stage	9.91
			3 <sup>rd</sup> Stage	10.10
			4 <sup>th</sup> Stage	10.33

Example 8:

Closed Circuit Design RO water reuse application (Single Stage, Fortilife CR100, 5 X 5)

Recovery: 90.5%, Feedwater Temp 18.3 °C

	Feed pH	Concentrate pH	Permeate pH
ASTM Method	4.45	N/A	-
Membrane Manufacturer Projection		4.4	4.5
AWC Proton <sup>®</sup> Projection		4.07	4.48
Actual		4.00	N/A





## V. DISCUSSION

In reviewing the data, it is evident that most membrane manufacturers appear to be using the  $\text{HCO}_3^-/\text{CO}_2$  equilibrium model, and that their calculated concentrate pH is almost always higher than the value measured onsite. The exception was the Dupont WAVE software which closely matched our calculated results and pH values measured onsite for most cases. However, the concentrate and permeate pH predictions for the second pass RO (Feed pH ~10) were very different than those measured onsite, while the AWC<sup>®</sup> Proton<sup>®</sup> software matched closely to onsite measurements. The same was true for the concentrate pH of the CCRO projection with a low feed pH of ~4.5. This suggested that while their model likely considered for various weak acid species, it did not account for hydronium and hydroxide ion rejection or diffusion across the membrane.

It is worth noting that we do not have specific information on the properties of every membrane model. The AWC<sup>®</sup> Proton<sup>®</sup> software assumes a certain relationship between sodium chloride rejection and that of other ions for different classes of membranes. Despite the generalized assumptions that we make, our pH in the concentrate was consistently within the margin of error of the onsite pH reading, even predicting cases where the pH of the concentrate was lower than that of the feed. The high buffering capacity in the concentrate allows for a significant amount of error without impacting the calculated pH reading. This only highlights the weakness of the  $\text{HCO}_3^-/\text{CO}_2$  equilibrium model since the membrane manufacturer software presumably calculate ion rejection very accurately and yet failed to predict correct concentrate and permeate pH values.

It is important to highlight the importance of using charge balance to validate a water analysis received from an environmental lab, as we regularly find many to be very imbalanced. Many industrial reuse applications contain extremely high concentrations of organic acids that can also lead to incorrect osmotic pressure calculations if not properly considered. The majority of membrane projection software now offer automatic charge balancing, discouraging the user from putting any thought into the process, and compounding the error when a poorly performed water analysis is input. Some offer the option of simultaneously balancing all the anions or all the cations, thereby completely changing the water quality and rendering the projections useless from a scaling prediction standpoint. Working with a correctly balanced water quality is essential for correctly predicting brine pH and scaling potential.

The permeate pH values calculated by the AWC<sup>®</sup> Proton<sup>®</sup> software were not as close to the measured values as those calculated for the brine pH. This is because RO permeate contains such a low concentration of buffering ions, that just 1 ppm of  $\text{HCO}_3^-$  (or any other dominant weak acid) would cause a significant variance in pH. The permeate pH is therefore sensitive to membrane age, batch to batch manufacturing variations in membrane properties, any incidents that may have caused surface abrasion (or delamination) of the membranes, deterioration of salt rejection due to frequent or aggressive chemical cleaning, and intersystem temperature increases introduced by pump heat due to friction and hydraulic losses. In calculating the permeate pH, an error is also introduced by our generalized assumptions on how various ions are rejected. However, despite these assumptions, our calculated permeate



pH values were consistently closer to actual measured values than those of the membrane manufacturers.

## V. CONCLUSION

The HCO<sub>3</sub>/CO<sub>2</sub> model used in the projection software of most membrane manufacturers and antiscalant suppliers is unreliable. It predicts excessively high pH values that result in high scaling calculations, leading to recommendations for unnecessary pH adjustment or excessively high antiscalant dosages. A model that considers for all weak acids, weak bases, ion complexes, free hydronium and hydroxide ions, and electroneutrality was found to consistently predict reliable concentrate and permeate pH values when compared to onsite measurements. The ability to account for organic acids, where the concentrations and pKa values were known, was also important as they could significantly impact pH. The model was made more accurate by accounting for rejection of various ion species determined empirically and assumed to be consistent within membrane categories from different membrane manufacturers.

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