Coupling mass transport and chemical equilibrium models for improving the prediction of SWRO permeate boron concentrations

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HIGHLIGHTS

► A new reverse-osmosis boron permeation numerical simulation method is presented.
► The method couples classic transport methods with chemical equilibrium models.
► Simulation results are shown to better match measured B permeate concentrations.
► A prominent difference from classic models is in pH calculation throughout RO path.

ABSTRACT

A new simulation approach is presented for predicting boron concentrations in the product water of seawater reverse osmosis operations. The new ( numerical) approach links traditional mass-transfer models (the solution-diffusion transport approach and the concentration polarization film-layer model) with full aqueous-phase thermodynamic species characterization, performed by chemical equilibrium software (PHREEQC), based on the Pitzer approach. The new approach results in a more accurate calculation of the boric acid (B(OH)₃) molar fraction which develops close to the membrane wall, on the feed side, thereby improving the prediction accuracy of B(OH)₃ permeation. Specifically, acknowledging that the pH value of the feed invariably changes as seawater brine progresses through the membranes’ train, calculation of this pH change, as performed in the new approach, enables a more physically-accurate and better simulation of the boric acid fraction. The new approach is shown in the paper to result in a prediction that matches better empirical results obtained from the operation of a pilot-scale SWRO plant, as compared to the traditional approach.

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1. Introduction

Low B concentration, in the range 0.3–0.5 mg B/l, is required nowadays in many seawater desalination plants, in which the product water is planned to be used for irrigation, either directly or as treated wastewater. When the product water is intended solely for domestic consumption, B concentration in the range of 0.75–1 mg B/l is often required. Under typical SWRO (sea water reverse osmosis) operation conditions, i.e. pH in the range 7.0–8.0 and a recovery ratio of 40%–50%, the B concentration in the 1st pass permeate ranges between 0.8 and 1.6 mg B/l. Further B Removal is commonly obtained via a post-treatment stage comprising of either partial 2nd RO pass, an ion exchange step or a combination of the two. As recognized by several authors [1–4], higher B removal in the 1st pass has a potential for eliminating or significantly reducing the post-treatment B removal step, resulting in decreased plant complexity, reduction of capital expenses, and in some cases [3] also reduction in operational expenses. Enhanced B rejection can be achieved by applying membrane elements characterized by high rejection towards B(OH)₃. However, applying these membranes results in lower permeate flux and higher overall energy consumption [2]. Breaking this tradeoff requires a major change in membrane production practices [5]. Another approach is to raise the pH of the seawater feed with the aim of reducing the concentration of the poorly-rejected B(OH)₃ species. This approach was tested at the pilot and full-scales and shown to be cost-effective in achieving drinking water B requirements (0.75–1 mg B/l) without a need for a post-treatment step (i.e. single-pass operation) at the pH range 8.4–8.5 [1,3,6]. For achieving B thresholds for irrigation (0.5–0.3 mg B/l) it was shown that feed pH should be increased to pHe8.8–pH9.3 [6]. The risk of CaCO₃ scaling at high pH and the relatively high dose of costly strong base required to achieve it, are currently limiting the implementation of the latter approach [4]. A recently developed novel approach for single pass B removal bypasses these limitations by removing most of the inorganic carbon (i.e. the sum of the three dissolved carbonate species, denoted C₃) in a pre-treatment step [6]. The choice of the most cost-effective B removal
process and its optimal design require a reliable cross-membrane transport simulation procedure, which produces accurate results in a wide range of operational conditions and feed water compositions. Process design commonly includes a safety margin of 0.1 mg B/l in the product water; therefore, B permeation simulation should strive to provide an accuracy of at least 0.1 mg B/l, to be valuable from the design standpoint. This goal, as shown further in the text, can only be achieved by considering the full set of chemical processes which affect B speciation near the membrane wall, on the feed side. Following seawater evaporation were successfully predicted by this model [18]. The Pitzer equations and the data-base incorporated in PHREEQC are largely based on the 25 °C Harvie–Moller–Weare aqueous model [19]. This model differs from the classic Pitzer treatment (which only considers interactions between pure ions), because it takes into account the formation of several ion-pairs, e.g. CaCo$_3$, MgCo$_3$. Solubility of various minerals and precipitation of solids following seawater evaporation were successfully predicted by this model [19]. Pitzer-based interaction parameters, specific for B species, were later on added to the Harvie–Moller–Weare model and verified experimentally by Felmy and Weare [20]. These parameters were also embedded in the PHREEQC data base. In Felmy and Weare’s model, the ion-pairs MgB(OH)$_4$ and CaB(OH)$_4$ were treated as separate species, while interactions of borate with Na$^+$ and other ions were embedded in the Pitzer parameters. Polyborate ions, which are also considered by this model, are negligible (rejection >99%), as compared to that of boric acid [14]. Therefore, accurate determination of the B(OH)$_3$, molar fraction from the total boron ($\phi_{boric}$) concentration is essential for successful simultaneous prediction of permeate B concentrations. The Boric acid fraction can be calculated for a given pH value using Eq. (2), according to the apparent dissociation constant ($K_{d}$), which is defined by the boric acid concentration, the total borate species concentration and pH (see Eq. (3)). Empirical equations can be used to determine $K_{d}$ for given temperature and salinity values.

\[
B(OH)_3 + H_2O\rightarrow B(OH)_4^- + H^+
\]  
\[
\phi_{boric} = \frac{10^{-\text{pH}}}{10^{-\text{pH}} + K_{d}}
\]  
\[
K_{d} = \frac{[B(OH)_3]}{[B(OH)_4^-]} \frac{10^{-\text{pH}}}{10^{-\text{pH}} + K_{d}}
\]

Mane et al. [10], following the work of Hyung and Kim [9], used the equation published by Edmond and Gieskes in 1970 (Eq. (12)) [15], developed for a large range of salinities (up to ~90 g/kg), to calculate $K_{d}$ value for use within pilot and full-scale SWRO simulations. As acknowledged by [9] and [10] $K_{d}$ and $\phi_{boric}$ change along the membranes’ train, as a function of the recovery ratio and CP. In contrast, Hung et al. [12] used Dickson’s equation [16], developed for salinities up to seawater, to determine $K_{d}$. All the simulation works cited above [6–12] are based on the assumption that the pH of the brine, from the raw seawater to the brine at the outlet of the SWRO step, is constant. However, in contrast with this assumption, significantly different pH values are measured regularly at the feed and brine in SWRO applications [1,2]. Acknowledging that the pH value changes along the feed water (brine) path, accurate determination of $\phi_{boric}$ at each numerical point requires recalculation of the pH value at each step throughout the simulation. This insight was embedded in this paper by coupling the geochemical software PHREEQC, developed by the U.S. geological survey (USGS) organization [17] to a rather simple membrane transport model, programmed in MATLAB®. PHREEQC implements the Pitzer approach to model chemical equilibrium processes in highly concentrated electrolyte solutions [18]. The Pitzer equations and the data-base incorporated in PHREEQC are largely based on the 25 °C Harvie–Moller–Weare aqueous model [19]. This model differs from the classic Pitzer treatment (which only considers interactions between pure ions), because it takes into account the formation of several ion-pairs, e.g. CaCO$_3$, MgCO$_3$. Solubility of various minerals and precipitation of solids following seawater evaporation were successfully predicted by this model [19]. Pitzer-based interaction parameters, specific for B species, were later on added to the Harvie–Moller–Weare model and verified experimentally by Felmy and Weare [20]. These parameters were also embedded in the PHREEQC data base. In Felmy and Weare’s model, the ion-pairs MgB(OH)$_4$ and CaB(OH)$_4$ were treated as separate species, while interactions of borate with Na$^+$ and other ions were embedded in the Pitzer parameters. Polyborate ions, which are also considered by this model, are negligible in seawater and SWRO brines where B$_{t}$<22 mg B/l [14]. Among its many features, PHREEQC can simulate the changes in speciation induced by the addition or extraction of a certain phase from solution (i.e. irreversible reaction model) [17]. This ability was utilized in the current work to simulate the gradual changes in the brine solution chemistry, emanating from H$_2$O and B(OH)$_3$ permeation through the membrane. B speciation is

### List of symbols

- **A**: Membrane’s Active area
- **B$_{Tb}$**: B concentration in the feed bulk stream
- **B$_{Tm}$**: B feed concentration close to the membrane wall
- **B$_{Tp}$**: B concentration in permeate
- **BTpchaccum**: Accumulated B concentration in permeate
- **CB**: Total concentration of solutes in the feed bulk stream
- **CM**: Total concentration of solutes close to the membrane wall
- **Cl**: Chlorinity
- **d**: Feed channel height
- **fB**: B cross membrane flux
- **fW**: H$_2$O cross membrane flux
- **KB**: Mass transfer coeficient of salt
- **k**: Mass transfer coeficient of B
- **L_B**: Permeability coeficient of B
- **L_W**: Permeability coeficient of H$_2$O
- **P**: Hydraulic pressure
- **Q_p**: Permeate flow rate
- **r**: Recovery ratio
- **S**: Salinity
- **T**: Temperature
- **U**: Feed cross-flow velocity
- **ΔB**: Permeated B mass in a single iteration
- **ΔW**: Permeated H$_2$O mass in a single iteration
- **Øboric**: Molar fraction of B(OH)$_3$ from total B
- **ψ**: The osmotic coefficient of water

The osmotic coefficient of water interacts with other cations, namely Na$^+$, Mg$^{2+}$ and Ca$^{2+}$ to form weakly associated ion pairs [13]. B species distribution and hence B permeation, are strongly pH dependent. At pH>10.5 the dominant species is the borate ion, while at pH<7, boric acid prevails. The permeation of borate (including cation-borate ion-pairs) via RO membranes is negligible (rejection >99%), as compared to that of boric acid [14]. Therefore, accurate determination of the B(OH)$_3$, molar fraction from the total boron ($\phi_{boric}$) concentration is essential for successful simultaneous prediction of permeate B concentrations. B species distribution and hence B permeation, are strongly pH dependent. At pH>10.5 the dominant species is the borate ion, while at pH<7, boric acid prevails. The permeation of borate (including cation-borate ion-pairs) via RO membranes is negligible (rejection >99%), as compared to that of boric acid [14]. Therefore, accurate determination of the B(OH)$_3$, molar fraction from the total boron ($\phi_{boric}$) concentration is essential for successful simultaneous prediction of permeate B concentrations. B species distribution and hence B permeation, are strongly pH dependent. At pH>10.5 the dominant species is the borate ion, while at pH<7, boric acid prevails.
shown to be affected by changes in pH which were not considered in previous works and result in significantly different predictions of B concentrations in the permeate water. The results of the new simulation approach are shown in this paper to better match the measured permeate B concentrations.

2. Simulation algorithm

2.1. Description of the coupled modeling approach

The simulation approach presented in this work comprises coupling of RO membrane-transport models, which can be applied in any mathematical programming language, with chemical equilibrium models, which requires the use of specialized software, backed up by a large database. The coupled models exchange information with each other, increasing the accuracy of the data on which the simulation is based, as it proceeds. Currently, such coupled approaches are applied mostly in cutting edge modeling of hydro-geochemical processes [21,22]. Although a reaction-transport approach was already suggested for scaling risk assessment in thermal desalination applications [23], this work, to the best of the authors’ knowledge, is the first attempt to use it for RO transport simulation. In the general procedure of SWRO simulation by the coupled approach, water and solute transport data, as well as CP factors, are delivered from the RO model to the chemical equilibrium model, which uses it to perform a full speciation of the solutes near the membrane wall. The concentrations of the relevant species near the membrane wall are then sent back to the RO model, where they are used for the calculation of new transport data.

In this work, the code implementing the RO model was written in MATLAB®, while the chemical equilibrium model was solved by the PHREEQC software. For robustness and simplicity, water and B transport were calculated as a function of the water recovery ratio, using the solution–diffusion and CP film layer models.

2.2. The numerical procedure

As shown in Fig. 1, a solution for the water flux ($J_w$) and the concentrations in the CP layer ($C_m$) at each discrete point of water recovery ($r_i$) were primarily obtained by the MATLAB® program. This solution was inserted as input to the B transport simulation, which, in turn, predicted the B permeate concentration at each predefined recovery point. For SWRO it is safe to assume that the minute permeation of solutes ($\leq 1\%$) has a negligible effect on the permeated water flux. In such case, the equations describing water transport are reduced to Eqs. (4) and (5), which were solved simultaneously to obtain the water flux ($J_w$) and CP layer concentration ($C_m$).

$$J_w = L_{wi}(P - \Phi_m C_m RT) \quad (4)$$

$$\frac{C_m}{C_{bi}} = \exp \left( \frac{J_w}{k_i} \right) \quad (5)$$

The salt bulk concentration ($C_{bi}$) i.e. the bulk salinity, was determined directly from the recovery value using the expression $C_{bi} = C_{bi0} / (1 - r_i)$. The salt mass transfer coefficient ($k_i$) was calculated

![Flow-chart describing the numerical algorithm developed for implementing the coupled simulation approach.](image-url)
from the flow velocity ($U_i$), the feed channel height ($d$), the temperature ($T$) and the bulk salt concentration at each point, using empirical equations obtained from [24]. The osmotic coefficient in the CP layer ($\Phi_{fl}$) was initially calculated according to the empirical equation for seawater [25], using the bulk salt concentration and was subsequently corrected by an inner loop, as shown in Fig. 1. Once the values of $J_{w}$ and $C_m$ were calculated for all recovery values, the water transport simulation had terminated and the B transport simulation began.

A solution containing the composition of solutes in the feed, dissolved in 1 kg·H$_2$O (i.e. 55.56 moles of H$_2$O) was defined in PHREEQC. In each iteration, the MATLAB code calculated the B concentration in the membrane surface ($B_{(m)}$) using the film-layer model (Eq. (6)). Subsequently, the number of water moles ($\Delta w_i$) and B(OH)$_3$ moles ($\Delta B_i$) which needed to be extracted from the initial solution to reach the congruent salt and B concentrations were determined by mass balances (Eqs. (7), (8)).

\[
\frac{B_{(m)} - B_{p}}{B_{(m)} - B_{p}} = \frac{f_i}{k_i}
\]  
\[
\Delta w_i = 55.56 \times (1 - C_{10}/C_{m})
\]  
\[
\Delta B_i = B_{T20} - B_{T30}(C_{SO}/C_{m})
\]

This information was sent to the PHREEQC program, which simulated the solute concentrations and B permeation using the software’s built-in reaction model. PHREEQC then calculated the entire solution speciation according to the Pitzer/Harvey built-in reaction model. PHREEQC then calculated the entire solution chemistry in the CP layer, such as pH or B species distribution at any specific water recovery value, was stored. The molar fraction of boric acid out of the total B concentration ($\Phi_{boric}$) was sent back to MATLAB, which, in the following order, computed the discrete permeate concentration of $B_{(T_{pi+1})}$ using the solution–diffusion model (Eq. (9)) and obtained the accumulated permeate concentration ($B_{paccum(i+1)}$) and bulk concentration in the next recovery point ($B_{(T_{pi+1})}$) using mass balance (Eqs. (10), (11)).

\[
J_{B_{i+1}} = J_{B_{i+1}}B_{p_{i+1}} + J_{B_{p_{i+1}}} \Phi_{boric}B_{(m)} - B_{p_{i+1}}
\]  
\[
B_{paccum(i+1)} = \frac{1}{r_{i+1}} \sum_{i=1}^{r_{i+1}} (r_{i+1} - r_{i})B_{p_{i+1}}
\]  
\[
B_{(T_{pi+1})}(1 - r_{i}) = B_{T_{i}}(1 - r_{i}) - B_{p_{i+1}}(r_{i+1} - r_{i})
\]

The mass transfer coefficient for B ($k_B$) was calculated by the expression $k_B = k_i / 0.97$ [7]. For obtaining Eq. (9) it was assumed that all the dissolved B species in the permeate were in the form of B(OH)$_3$, which is practically true due to the low pH prevailing in RO permeates as a result of the passage of CO$_2$(aq) and B(OH)$_3$ through the membrane.

## 3. Methods

### 3.1. Evaluation of permeability constants and model input parameters

The permeability constants $L_m$ and $L_p$, required for the simulation, were evaluated from the membrane performance at standard test conditions (32,000 ppm NaCl, 5 ppm boron, 55 bars, 25 °C, 8% recovery and pH 8), as supplied by the manufacturer [26]. The water permeability coefficient ($L_w$), was derived from Eq. (4), based on average parameters, as follows: (1) the water flux was calculated from the expression $J_w = Q_w/A$, where $Q_w$ is the permeate flow rate and 'A' is the active membrane area; (2) $C_{m}$ was calculated by an empirical expression for the average concentration polarization factor in the first pass recovery B rejection, by high pH operation of the SWRO step [6]. High pH was enabled by an acid-stripping pre-treatment step, aimed at removing 92–96% of the inorganic carbon. Simulation results were tested by comparing them with empirical results obtained from operating a pilot system, which is described in [6], comprising a single SWRO 4" element (DOW’s SW30HRLE-4040). The input parameters for the simulation, shown in Table 1, are consistent with the experimental conditions in [6], within the boundaries of measurement accuracy.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Input parameters used in the numerical simulation.</th>
</tr>
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<tbody>
<tr>
<td>$S_{feed}$</td>
<td>$x$</td>
</tr>
<tr>
<td>g/kg</td>
<td>m/s</td>
</tr>
<tr>
<td>38.4</td>
<td>9.33e-7</td>
</tr>
</tbody>
</table>

In the simulation presented in this work, only the permeation of boric acid species was considered, while borate permeation was neglected for the purpose of simplicity. The total rejection of B at pH 11, which is to all intents and purposes the rejection sum of B(OH)$_4^-$ in its free and complexed forms (i.e. total borate), was shown elsewhere to be >99% [14]. Assuming 99.2% rejection for total borate and pH8.6, for example, the contribution from total borate permeation to the overall B permeate concentration would be as low as ~0.014 mg B/L. Having said this, borate permeation simulation can be easily included in the coupled approach, provided that the permeability constant for borate is available. Since the most significant driving force for B permeation is the concentration gradient between boric acid in the feed-side membrane wall and in the permeate, this value was determined in each simulation step. This calculation required the estimation of $\Phi_{boric}$ for different, gradually increasing salinities, which is not a simple task due to the complexity of seawater speciation and chemical interactions. Marine chemistry specialists often use the empirical equation developed by Dickson [16], which is based on rigorous electrochemical measurements and calculations.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Feed composition used as input in the simulation. Concentrations appear in mg/kgH$_2$O.</th>
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</thead>
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<tr>
<td>Cl$^-$</td>
<td>Na$^+$</td>
</tr>
<tr>
<td>21200</td>
<td>11800</td>
</tr>
</tbody>
</table>

Spiral wound modules [27], $C_m = C_s \exp(0.07r)$, where 'r' is the recovery ratio in a single element; and (3) the osmotic coefficient ($\Phi_{fl}$) and $\Phi_{boric}$ in the NaCl solution were obtained from Pitzer's equations, as solved in PHREEQC. B permeability coefficient ($L_p$) was then derived from Eq. (9). B$_w$ was determined from the feed concentration and reported B rejection. The simulation was based on a new approach for achieving single pass B removal, by high pH operation of the SWRO step [6]. High pH was enabled by an acid-stripping pre-treatment step, aimed at removing 92–96% of the inorganic carbon. Simulation results were tested by comparing them with empirical results obtained from operating a pilot system, which is described in [6], comprising a single SWRO 4" element (DOW's SW30HRLE-4040). The input parameters for the simulation, shown in Table 1, are consistent with the experimental conditions in [6], within the boundaries of measurement accuracy. The feed composition, typical Mediterranean seawater, shown in Table 2, was used as an input solution in the PHREEQC. B feed concentration was similar to that appearing in [6], while the inorganic carbon concentration was low due to a decarbonation pre-treatment step, following the process described in [6]. In the pH range applied in both simulations and experiments, the CO$_2$ concentration was very low and its permeation was thus neglected in the simulation. Since the system operated in a single module recirculation mode, with the concentrate passing through a high pressure pump in each cycle, pressure drop and cross-flow velocity decline were also negligible. The neglected parameters described above can be easily incorporated into the model for simulation of systems with different membrane arrays, e.g. full scale. The pH value of the feed water is reported in this paper in the NBS (National Bureau of Standards) scale and is thus subjected to measurement errors in the order of 0.08 pH units (see elaboration in the Results and discussion section).
is considered very accurate for seawater and estuary waters in the salinity range 5–45 g/kg. However, for higher salinities, as encountered in SWRO desalination brines, this equation is merely an extrapolation (see Fig. 2). Moreover, the dissociation constants of boric acid, to which Dickson’s equation was fitted, were originally measured with respect to a different pH scale (the seawater scale). Measurements of seawater pH in this scale require a different calibration procedure, and may yield results which are lower by >0.1 pH units, as compared to measurements obtained from the commonly used pHNBS (calibration with dilute NIST pH standards) scale. Thus, introducing the pHNBS value into Dickson’s equation results in underestimation of the \( \phi_{\text{boric}} \) value, and therefore in underestimation of the predicted B permeation values. Eq. (12), proposed by Edmond and Gieskes [15], is better suited for obtaining \( K_b' \) at high salinities, since it was fitted from measurements made in the salinity range 6–95 g/kg. Eq. (12) was originally presented in terms of \( T(K) \) and chlorinity (\%Cl), which can be converted to salinity (\%S) by the term \( \%S = 1.80655 \%\text{Cl} \).

\[
pK_b' = 2291.90/T + 0.017567T - 3.3850 - 0.32051(5/1.80655)^{1/3} \tag{12}
\]

At this point in the text, the readers are referred to a typo error in Eq. (12), as it was presented in [9]. This typo was repeated also in later publications of this research group [1,3] and also in a review paper [14]. In these papers, the multiplication by the temperature was dropped out of the second term, leaving only the number 0.01756, an error which results in large inaccuracies in the determination of \( pK_b' \). Eq. (12) was fitted to data obtained using the pHNBS scale, which is subjected to uncertainties resulting from the difference in the liquid junction potential between the NBS dilute buffer and the concentrated measured solution. In seawater, the pH error stemming from this phenomenon is estimated to be ~0.08 [28] and is expected to increase at higher salinities, e.g. SWRO brines. In Fig. 2, the \( \phi_{\text{boric}} \) value in the CP layer obtained by the two empirical equations mentioned above and the \( \phi_{\text{boric}} \) value obtained by the coupled approach are plotted as function of the recovery ratio, considering feed seawater pH of 8.6. The gaps between the curves appearing in Fig. 2 are only partly related to incongruent pH scales and pH measurement errors.

The distinctive \( \phi_{\text{boric}} \) value, which was obtained by the new simulation approach (i.e. by PHREEQC), was mainly the result of changes in the feed pH, as the solution becomes concentrated due to the effects of CP and of \( H_2O \) permeation (see Fig. 3). pH change on the feed side was previously studied mainly with connection to \( \text{CaCO}_3 \) scaling [29], but was largely ignored thus far in works addressing B rejection. Any change in the acid–base species distribution, occurring on the feed side during SWRO, will result in a counter reaction which has the potential to affect the pH value. For example, permeation of the weak acids \( \text{CO}_2 \) and \( \text{B(OH)}_3 \), while their conjugate bases, \( \text{HCO}_3^- \), \( \text{CO}_3^{2-} \) and \( \text{B(OH)}_4^- \) are rejected by the membrane, results in an association between hydrogen ions and the basic species, and therefore in increase in pH. Contrary to this process, the concentration of feed solute induces a decline in the activity of basic species due to increased ionic interactions, while the activity of uncharged acidic species is increased due to the “salting out” effect. The counter reaction for the latter is proton dissociation. In other words, the shift of \( K_b' \) to lower values under increased salinities is counteracted by the decline in pH. As shown in Fig. 3, the simulated changes in pH start immediately after the feed solution enters the membrane module and is subjected to CP, resulting in the initial increase and the relatively moderate decline in the \( \phi_{\text{boric}} \) value, as compared to the \( \phi_{\text{boric}} \) value obtained from Eqs. (12) and (2), which assume constant pH throughout the brine path.

As shown in Fig. 4, underestimation of the \( \phi_{\text{boric}} \) value may result in underestimated B permeation prediction. The simulation results for the conventional and the coupled approaches are compared in Fig. 4 with results obtained in pilot-scale experiments (reproduced from [6]). Better predictions of the experimental results were clearly obtained by the coupled approach for almost every initial feed pH (at initial pH9.25 the predictions were similarly close to the measured values) and recovery ratios. The improvement in the ability of the simulation to predict the experimental B permeate concentrations is particularly significant at the high recovery ratio range, where the increase in \( \phi_{\text{boric}} \) value (see Fig. 2) is accompanied by a higher total B concentration on the feed side. Consequently, the difference between the two simulations in Fig. 4 is the largest at the recovery endpoint (43%). The largest deviation from experimental results occurred at the point of the highest B permeation (pH 8.1, recovery ratio ~43%) for both simulations. However, the traditional approach deviated 0.14 mg B/l from the measured B permeate concentration while the coupled approach deviated merely 0.04 mg B/l. At pH 8.6, the coupled simulation predicted B permeation within all the recovery ratio range with remarkable accuracy, while the conventional approach resulted in a deviation of ~0.12 mg B/l.

The recovery endpoint is probably the most significant point, since it represents the water quality at the outlet of the SWRO membrane train. Nevertheless, accurate prediction of B concentration at lower recovery values is also important, for example, for more optimal design of a partial 2nd pass step, if required. Both simulations, used for constructing the curves in Fig. 4, were based on the same transport model, numerical procedure and input parameters, as described in Section 2. The only difference was in the method used for the estimation of \( \phi_{\text{boric}} \) in each iteration, i.e. Eqs. (2) and (12) were used for obtaining the right hand side curve, and the coupled approach for obtaining the left hand side one. It is noted again that the simulation results were obtained using permeability coefficients derived under
standard test conditions. Future fine-tuning of these data may result in even higher prediction accuracy.

5. Conclusions

A new approach for the simulation of B permeation by RO membranes, which is based on coupling membrane transport and chemical equilibrium models, was developed, and compared with experimental results. Improved predictions were obtained by the coupled approach, as compared to previous works in which constant pH was assumed. This modeling approach, although applied in the current work for seawater, can be used to simulate B permeation with other RO feed water sources as well, e.g. brackish ground water, geothermal water, oil and gas produced water, urban and industrial wastewaters, etc. Further work is required to study the potential applications of the coupled approach. Incorporation of PHREEQC’s thermodynamic calculation procedure into external codes written in other programming languages (MATLAB included), is becoming more accessible because of designated modules released by the USGS [30]. Automation of the coupled procedure, which was performed manually in this work, will enable running the simulation with varying feed compositions and analyzing the effect of more parameters, temperature for example, within a wide range of operational conditions. The largest uncertainty associated with the chemical equilibrium model used in this approach lies probably in the measured pH introduced to it. Development of a pH measurement procedure, both consistent with the model and reproducible, may further improve the simulation predictions. The suggested simulation approach has the potential to improve future understanding regarding the way chemical reactions in the aqueous phase, occurring in the brine during RO operations, affect system performance.

Acknowledgment

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References