TWO-SCALE MODELLING OF THE CONCENTRATION POLARIZATION IN A REVERSE OSMOSIS MEMBRANE

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Abstract

In the design and control of reverse osmosis desalination plants, the clean water flux, which passes through the membranes, is the most important variable. Flux depends on several parameters, such as the membrane permeability or the temperature, but mainly on the salt concentration on the membrane surface. The salt concentration is easily measured in the bulk of the feed, but not on the membrane surface, where it should be estimated. The concentration polarization creates an unwanted increase of the salt concentration between the bulk side and the membrane surface. The polarization effect is due to the convective transport of salt molecules by the water flow to the boundary layer of the membrane, and their subsequent blockage by the membrane itself. A correct estimation of the concentration polarization is fundamental to predict the clean water flux, and finally, to be able to carry out a good design and control of the desalination plant. Several models have been proposed in the literature to calculate the concentration polarization (or the salt concentration on the membrane surface). This paper presents a new model, which aims to solve some of the disadvantages of the previous models.

Keywords

Two-Scale Modelling, Dynamic Modelling, Brownian Motion, Reverse Osmosis Desalination, Concentration Polarization.

Introduction

Over the last twenty years, Reverse Osmosis (RO) has become the main desalination technique, all around the world, to produce drinkable water from brackish and sea water. Around 50% of desalination plants currently use RO technology and most new plants are designed using this technology. Advances in RO membrane materials, and mainly in the recovery of energy, have considerably decreased the price of the clean water, and the energy consumption of RO desalination plants has reached values lower than 3 kWh/m^3, which is several times lower than the consumption 10 years ago, and is only slightly greater than the thermodynamic minimum energy consumption (around 1 kWh/m^3), which is the unimproved limit of consumption. Nowadays, the two main approaches of the state-of-the-art in desalination plants are optimization of the energy consumption (see (Bartman et al. 2010, Penate and Garcia-Rodriguez, 2011, Zafra-Cabeza et al 2011, Zhu et al. 2010)) and dynamic modelling of the desalination plants (see (Bartman et. al 2009A, Bartman et. al 2009B, Gambier et al. 2007)). A correct dynamic model is fundamental in order to design advanced control strategies

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for a desalination plant and to minimize the energy consumption.

The RO process basically consists of the extraction of part of the water molecules from the feed water through a membrane, which the molecules are forced to go through. Owing to the narrow size of the membranes, which makes it impossible for bigger particles, such as the salt molecules, to pass, the desalination is carried out. In order to force the water molecules to cross the membrane, the feed water pressure should be increased up to a value greater than the osmotic pressure of the feed flow, which depends on the salt concentration. Typical values of operation pressure are respectively 30 - 60 bar for brackish and sea water. The RO process produces two different flows: a clean water flow, called permeate, obtained from the water molecules that have crossed the membrane, and a rejected flow, called reject, formed by the rest of the molecules. The salt concentration of the permeate is not exactly zero, since a low number of salt molecules (less than 0.1%) are able to cross to the permeate, due to microscopic defects in the membranes. In any case, the salt concentration of the permeate is several times lower than in the feed flow, and in fact, lower than the required value for human consumption. So, the RO process should be followed by a slight, controlled re-mineralization. On the other hand, the salt concentration of the reject is very high, and the place where this flow is thrown out should be carefully studied, in order to avoid any possible degradation of the environment. Typical values of the permeate flow are, respectively, 75% and 45% of the feed flow for brackish and sea water. See (Alatiqi et al. 1999, Baker 2004, Wilf 2007).

Concentration polarization (CP) is the unwanted and inevitable effect of the increased salt concentration in the boundary layer, close to the membrane surface. Salt molecules are accumulated in the boundary layer, after being transported by the permeate flow, which crosses the membrane, and (the majority) being rejected by the membrane itself. CP is one of the most important factors influencing the permeate flow produced in RO desalination plants, due to the fact that the water flux and the scaling on the membrane surface are proportional to the osmotic pressure between both sides of the membrane; that is, to the salt concentration on the membrane surface (or to the CP). See (Bhattacharjee and Johnston, 2002, Hoek and Elimelech, 2003, Marinas and Urama, 1996). Typically, CP is modelled following the Film Theory (FT), which was developed by Michaels and others (Michaels, 1968; Porter, 1972). The FT model has several limitations, such as the lack of influence between the permeate flow and the boundary layer thickness, so new, more rigorous models have been proposed (Kim and Hoek, 2005; Song and Elimelech, 1995), which improve several aspects of the CP calculation. However, the FT model (maybe owing to its simplicity and popularity) is still the most applied model. This chapter presents a new Two-scale-based Modelling of the CP, which aims to improve several of the drawbacks of the previous models.

This work is organized as follows: The state-of-the-art of CP modelling is briefly described in the next section. Then, the two-scale model proposed in this work is presented, followed by the model validation and the parameter estimation. The paper ends with the conclusions and the bibliography.

CP modelling

Figure 1 qualitatively symbolizes the Concentration Polarization close to the membrane surface. The left and righthand sides of the figure symbolize, respectively, the feed side and the permeate side of the pressure vessel. The feed flow flows from bottom to top on the lefthand side, and the permeate flux (F_p) flows from left to right, crossing the membrane. The salt concentration increases from the bulk on the feed side (C_b), to the membrane surface (C_m), which belongs to the CP. Because the majority of the salt molecules are rejected by the membrane, the permeate concentration (C_p) on the permeate side is several times lower.

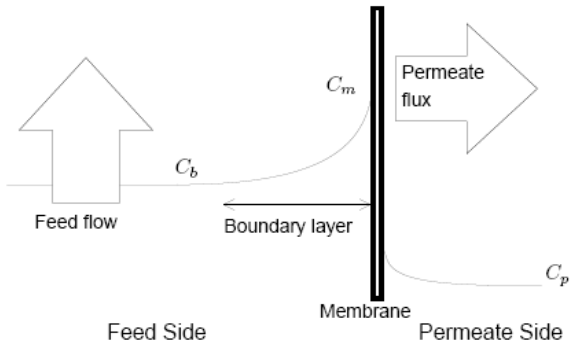

Figure 1. Concentration polarization.

In a desalination plant, bulk and permeate concentrations are easily measured with Redox and conductivity sensors at the input and output of the pressure-vessel train, but not the membrane concentration, which should to be estimated. Several models have been proposed to calculate the C_m: such as the Film Theory (FT) model (Michaels, 1968; Porter, 1972), the Retained Solute (RS) model (Song and Elimelech, 1995; Song and Yu, 1999) or the Convection-diffusion (CD) model (Kim and Hoek, 2005), which will be described next. On the other hand, notice that all the variables that appear in the CP problem (C_b, C_m, C_p, F_p, etc.) vary along the pressure vessels, as shown in figure 2. So, in order to calculate the total produced permeate flow, two possibilities are followed: (a) using an average value for the different variables between the inlet and the outlet of the pressure-vessel train (Eq. (1)) or (b), discretizing the pressure vessels into several elements and applying the chosen CP

model to each element. The first alternative is typically used in optimization problems (such as (Lu et al., 2006)), where the correct concentration profile is not critical, while the second one is used in detailed modelling and advanced simulation of RO membranes (such as (Senthilmurugan et al., 2005; Senthilmurugan and Gupta, 2006)).

$$\overline{C_b} = 0.5 \cdot (C_f + C_r) \tag{1}$$

Where C_f and C_r mean, respectively, the salt concentration in the inlet feed flow and in the outlet of the reject flow.

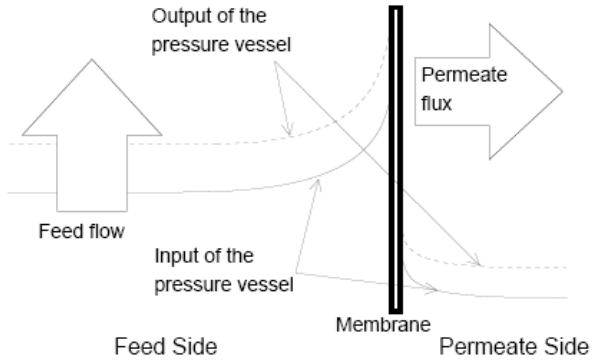

Figure 2. Concentration polarization along the length of the pressure vessel.

The most popular and commonly used model for CP calculation is the FT model, which is also the oldest one (Michaels, 1968). The FT model analytically integrates the local one-dimensional mass balance for salt particles, in the boundary layer close to the membrane surface, as can be seen in figure 3. Equation (2) shows the mass balance used in the FT model, where *D* means the diffusion coefficient.

$$\frac{\partial C}{\partial t} = F_p \cdot \frac{\partial C}{\partial x} - D \cdot \frac{\partial^2 C}{\partial x^2} \tag{2}$$

Assuming a steady state and taking into account that the total convective salt flow, which crosses the membrane, is $F_p \cdot C_p$, Eq. (2) could be simplified as follows:

$$D \cdot \frac{\partial C}{\partial x} - F_p \cdot (C - C_m) = 0 \tag{3}$$

Next, Eq. (3) is integrated over the boundary layer thickness (δ), (from x = 0 with C = C_b, to x = δ with C = C_m), assuming constant diffusivity:

$$\phi = \frac{C_m - C_p}{C_b - C_p} = \exp\left(\frac{F_p}{k}\right) \tag{4}$$

Where ϕ, which is called the CP module, is an adimensional coefficient that quantifies the CP, and k *(= D/δ)* means the mass-transfer coefficient from Fick's Law for molecular diffusion.

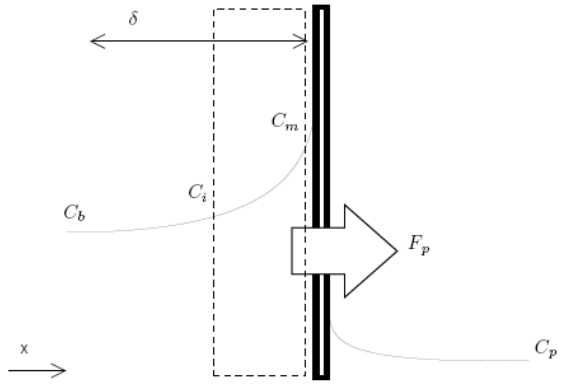

Figure 3. One-dimensional mass balance for salt particles.

Since that FT model was proposed by Michaels, the major effort in CP modelling has been focused on the calculation of *k*. From then on, several empirical and theoretical equations have been proposed in the literature. However, most of them are available only under laboratory conditions. For example, see (Davis, 1992; Evangelista, 1986; Probstein, 1994; Zydney and Colton, 1986).

Nowadays, the typical way to calculate k is to assume the dependence of k and F_p shown in Eq. (5), and then to estimate the parameters a and b for each particular desalination plant.

$$k = a \cdot F_p^{\,b} \tag{5}$$

There are several limitations to the FT model, such as the assumption that the boundary layer thickness (δ) does not depend on the permeate flux, the use of average parameters over the total pressure vessel in the majority of cases, and the assumption of time equilibrium. However, owing to its simplicity and that it gives reasonable predictions, especially for low flux and pressure conditions, it is the most widely used model.

As in the case of the FT model, the RS model (see Song and Elimelech, 1995) solves the CP problem by analytically integrating a mass-transfer for salt particles, but in this case, over two directions: parallel to the permeate flux and close to the membrane surface (axis x, as in the FT model), and parallel to the feed flux (axis y). Figure 4 shows the two-dimensional discretization over a spiral-wound module, where the mass balance is integrated. Assuming a known profile of pressure and osmotic pressure over the pressure vessel, which is the major limitation of this model, the FT model could be analytically integrated.

The CD model (Kim and Hoek, 2005) solves the two-dimensional mass balance for salt particles from figure 4,

coupled with the Navier-Stokes equations. This model should be integrated numerically, owing to the difficulty of the math equations. The CD model improves the prediction on permeate flow and CP for conditions of high pressure and flux, and is attractive due to the correct calculation of flows for realistic ranges in RO desalination plants. However, it can be improved in several aspects, such as the assumption of a steady state.

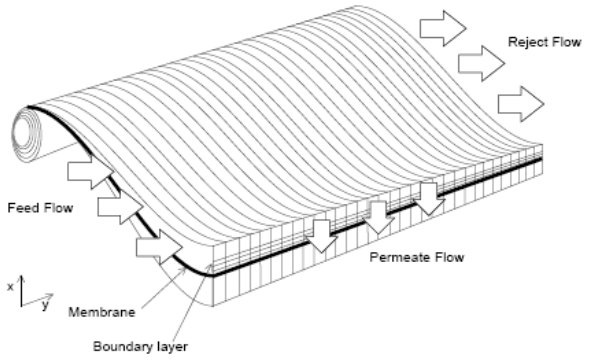

Figure 4. Two-dimensional mass balance for salt particles.

Two-scale CP model

The proposed modelling consists of a two-scale model that incorporates the dynamic calculation of the bulk concentration and the concentration polarization. On the one hand, the salt concentration of the bulk is calculated macroscopically along the membrane, from the feed flow and the outlet of the reject. In order to do this, the membrane is discretized in the axial direction into n_1 elements, parallel to the feed flow (*y* direction of figure 4), and the mass and momentum balances are carried out for each element as can be seen in Eq. (6) and (9).

$$\frac{\partial C_i}{\partial t} = \frac{\partial \left(Q_i \cdot C_i\right)}{\partial y} - F_{C\,i} \cdot \partial a \tag{6}$$

where the subindex $_i$ corresponds to the n_1 elements of the discretization in the *y* direction, *Q* means the water flow on the bulk side (at *y=0*, *Q* = feed flow, and at *y=L*, *Q* = reject flow), F_C is the salt flux that crosses the membrane in each discretization (and can be calculated as shown in Eq. (8)), and ∂a means the membrane area of each discretization.

The salt flux and water flux in each element can be calculated as shown in Eq. (7) and (8).

$$F_{p\,i} = A \cdot (\Delta P_i - (C_{m\,i} - C_p) \cdot \alpha) \tag{7}$$

$$F_{C\,i} = \frac{B \cdot (C_{m\,i} - C_p)}{F_{p\,i}} \tag{8}$$

where *A* and *B*, respectively, mean the water and salt permeability, ΔP means the different of pressure between the permeate and the feed side, and α is a coefficient that links the salt concentration with the osmotic pressure(embracing the temperature, the Van't Hoff coefficient, the ideal gas coefficient, etc) and C_m means the salt concentration on the membrane surface, which will be calculated next.

Several empirical and semi-empirical equations have been proposed in the literature to calculate the pressure drop of the feed side along the pressure vessel, as in Eq. (9), (Senthilmurugan et al., 2005).

$$P_i - P_{i-1} = a \cdot Q_i^{\,b} \tag{9}$$

Next, a new discretization is carried out in the boundary layer close to the membrane surface, in the direction parallel to the permeate flux (*x* direction of figure 4). The CP is modelled by a mixture between the Monte Carlo methods and the Langevin equations. See

On the other hand, concentration polarization in each element is calculated microscopically. A new discretization in the boundary layer close to the membrane surface is carried out in the radial direction (parallel to the permeate flow and perpendicular to the feed flow). Next, the concentration polarization is modelled by a mixture between the Monte Carlo methods and the Langevin equations. See (Jacobs, 2009; Chena and Kimb, 2004; Cecconi et al., 2005). In particular, the position of one salt particle is modelled as follows:

$$m \cdot x'' = F_{C\,i} - b \cdot x' + e \tag{10}$$

where *m* means the mass of the particle, *x* is the position of the particle, $F_{C\,i}$ means the convective flow that pushes the particle in the membrane surface direction), *b* is a parameter that depends on the opposition of the particle to be moved (by Stokes law), and *e* is a stochastic parameter that simulates the Brownian motion. In a general Langevin equation, *e* can be calculated as a Wein process by a Gaussian distribution with mean (μ) zero and variance σ^2. In the model proposed, the mean of the Gaussian distribution is not zero, but proportional to the salt concentration gradient in the radial direction (parallel to the permeate flow and the profile of concentration polarization) as shown in Eq. (11). See (Biagini et al., 2009; Huang, 2009):

$$\mu = \beta \cdot \Delta C \tag{11}$$

The calculation of the position of one single particle does not produce any useful result. However, by repeating the calculations for a huge number of particles (for example, 1 million), the average result is able to predict the concentration polarization.

Figure 5. RO pilot plant.

Model integration and parameter estimation

The proposed model requires five parameters: A, m, b, β, σ^2, which will be estimated in this section. The value of these parameters is the same for all n_1 elements. The parameter estimation was carried out using experimental data from a desalination pilot plant. The pilot plant, which produces $1 m^3/h$ of permeate flow, was specially designed for testing and experimentation and has a huge number of sensors, more than in a typical RO plant, as can be seen in figure 5. All the main parameters in the RO plant can be measured at different points of the plant. Sensors are managed from an OMRON PLC, and the data loading is carried out using OPC protocol. In order to correctly carry out the parameter estimation, several experiments were done to change the quality of the feed water, while also covering the entire range of pressures and flows allowed in the plant. However, it is not possible to measure the concentration, pressure or flow inside the pressure vessel, as these variables can only be measured at the inlet and outlet. Once enough experiments have been done and the data have been filtered and treated, it is possible to do the parameter estimation and the validation of the model. This is done by the minimization of a certain objective function, Eq. (12), which penalizes the difference between the measured and estimated permeate flow and concentration over time. The parameter estimation can be done using a simple nonlinear programming (NLP) algorithm, such as Successive Quadratic Programming (SQP).

$$J = \sum \left(F_{p\,measured}(t) - F_{p\,calculated}(t) \right)^2 + \\ + \sum \left(C_{r\,measured}(t) - C_{r\,calculated}(t) \right)^2 \tag{12}$$

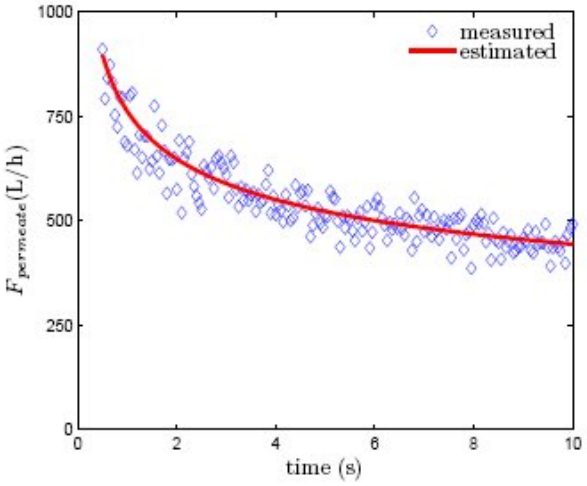

Figure 6. Measured and estimated permeate flow (L/h), during 10 seconds.

Figure 6 shows permeate flow, measured in the RO pilot plant, and estimated by the proposed model. The average error between measurement and estimated data is 14%. The calculated parameters for the specific pilot plant of figure 6 are: $A = 27$, $m = 9.1 \cdot 10^{-4}$, $b = 0.13$, $\beta = 0.33$, $\sigma^2 = 1.0 \cdot 10^{-2}$.

The integration of the proposed model requires a solution for Eq. (10), the number of elements (n_1) times the number of particles (around 1 million). This integration is very complicated and takes too much time, over 20 minutes. However, this time can be drastically minimized by an off-line math reduction (See Xie and Theodoropoulos, 2010). After the parameter estimation is done, a second step is carried out. The two-scale modelling is identified by a set of neuronal networks. After that, using the said neuronal networks, the model can easily be integrated (in less than 1 second).

Conclusions

A new two-scale modelling for the concentration polarization in RO desalination plants has been described. Next, the parameter estimation based on experimental data from a pilot plant has been carried out. Finally, the integration of the dynamic math model, using a math reduction based on neuronal networks, has been used.

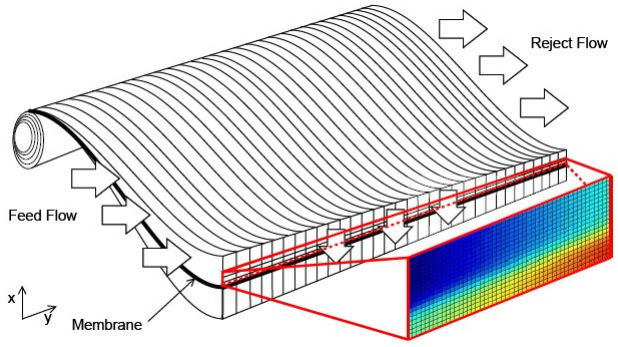

Figure 7. Discretization of the pressure vessel.

Finally, figure 8 displays the integration of the proposed model. The salt concentration is calculated in each element of the two discretizations (parallel to the feed flow, in *x* direction, and parallel to the permeate flow, in *y* direction). The matrices of figure 8 correspond to the salt profile at time 0, 2, 4, 6, 8 and 10 seconds, respectively. The elements of each matrix correspond to the elements of the two-dimension discretization of the boundary layer close to the membrane surface, as can be seen in figure 7. The lefthand side of the matrices corresponds to the feed flow and the righthand side to the outlet of the reject flow. The top side corresponds to the bulk and the lower side to the membrane surface. Notice how the salt concentration increases along the membrane (in the *y* direction, owing to the filtration of clean water); and how it increases in time, owing to the salt accumulation in the membrane surface.

Future work

As future work, we can emphasize the connection of the CP with several operation variables, specially the Specific Energy Consumption (SEC) and the membrane fouling. Besides, a dimensionless parameterization of the model should be carried on. See (Zhu et al., 2009).

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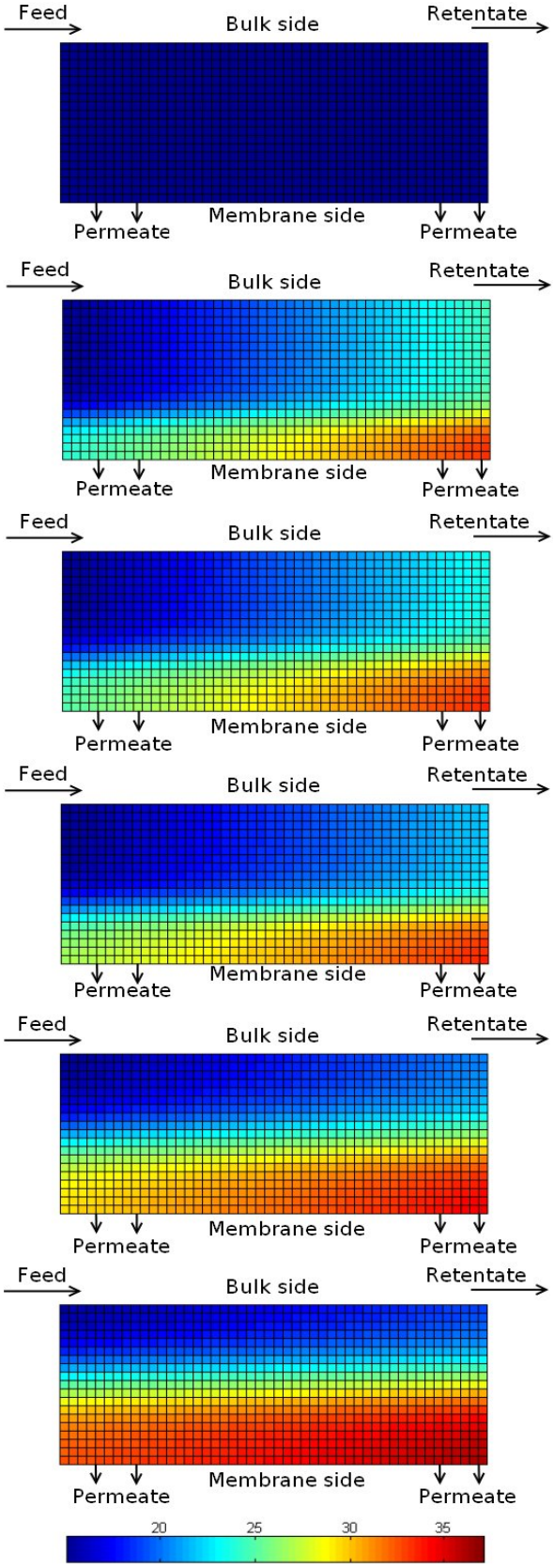

Figure 8. Salt concentration along the membrane, at time = 0, 2, 4, 6, 8, 10 seconds.

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