Supplementary Information
Large scale energy storage using multistage osmotic processes: Approaching high efficiency and energy density

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January 22, 2017

1 Multistage Reverse Osmosis Model

The salty water (sw) stream enters the RO part of the OES system, at a volumetric flow of $\dot{V}_{sw}$ and at environmental pressure P_0. As the PEX requires equal volumetric flow on both sides, the sw stream is split into $\dot{V}''_{sw}$ and $\dot{V}'_{sw}$, where $\dot{V}''_{sw}$ is equal to the volumetric flow of the brine (br) solution and $\dot{V}'_{sw}$ is equal to the volumetric flow of the fresh water (fw) stream. $\dot{V}''_{sw}$ stream is pressurized in a booster pump to overcome the pressure loss δP, before it is sent to the PEX, to exchange pressure between the br stream. The other $\dot{V}'_{sw}$ stream is pressurized using a high pressure pump to P_1^r and is then mixed back with the $\dot{V}''_{sw}$ stream to make $\dot{V}_{sw_1}$.

After being pressurized, the salty water (sw) stream $\dot{V}_{sw_1}$ enters the first membrane module (mm_1) where some of the fresh water (fw) crosses the membrane as $\dot{V}^r_{fw_1}$.The volumetric flow of the fw crossing the membrane is controlled by the hydraulic pressure ΔP_1^r across the membrane module, which we explain later for the i^{th} membrane module (mm_i) using the membrane effectiveness factor (Eq. 9).

We define a fw recovery ratio for a membrane module mm_i which describes how much fw is recovered from the sw stream entering the membrane module. All of the membrane modules have their own separate fw recovery ratio X. We describe this ratio and other properties for the i^{th} membrane module (mm_i). The fw recovery ratio for mm_i is defined as

$$X_i = \frac{\dot{V}^r_{fw_i}}{\dot{V}_{sw_i}} = \frac{\dot{V}_{sw_i} - \dot{V}_{sw_{i+1}}}{\dot{V}_{sw_i}} = 1 - \frac{\dot{V}_{sw_{i+1}}}{\dot{V}_{sw_i}} \tag{1}$$

where the sw stream entering the i^{th} membrane module (mm_i) is labelled as $\dot{V}_{sw_i}$; $\dot{V}^r_{fw_i}$ is the fw stream permeating mm_i, and $\dot{V}_{sw_{i+1}}$ is the resulting saltier sw stream leaving mm_i on the retentate side. The fw recovery ratio for RO is defined such that the X value for any RO membrane module is always less than or equal to 1. A X value close to 0 indicates no fw crosses the membrane layer, on the other hand, an X value close to 1 indicates 100% of the fw is recovered from the sw stream.

We use the salt rejection coefficient R defined for a membrane to calculate the salt crossflow, i.e. from sw to fw side. The salt rejection coefficient is broadly used in the membrane industry [1]. The salt rejection for all membrane modules is kept constant. It is generally defined as

$$R = \left(1 - \frac{C_{fw_i}}{C_{sw_i}}\right) \tag{2}$$

where C_{sw_i} is the molar concentration of the sw stream entering the membrane module and C_{fw_i} is the concentration of the fw stream permeating the membrane. As we know the molar salt flow in the sw stream entering the membrane module, we can find how much salt is left on the retentate side using the rejection coefficient, as

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well as find how much salt is passed on to the fw side. In multistage RO, a membrane module of length L is cut down to n membrane modules of length $\frac{L}{n}$ each. In the same way, we have assumed that the salt flow is distributed among the membrane modules, as the rejection coefficient value used for simulations are for a full membrane module.

The molar salt flow balance for streams leaving the i^{th} membrane module (mm_i) using R and salt distribution is described as,

$$\dot{V}_{sw_{i+1}} \text{ stream:} \qquad \dot{n}^s_{sw_{i+1}} = \dot{n}^s_{sw_i} - \frac{(1-R)\dot{n}^s_{sw_i}}{n}, \tag{3}$$

$$\dot{V}_{fw_i} \text{ stream:} \qquad \dot{n}^s_{fw_i} = \dot{n}^s_{sw_i} - \dot{n}^s_{sw_{i+1}} = \frac{(1-R)\dot{n}^s_{sw_i}}{n} \tag{4}$$

where $\dot{n}^s_{sw_i}$ is the molar flow of salt in the sw stream entering mm_i, $\dot{n}^s_{fw_i}$ is the molar salt flow in the fw stream that crossed the membrane, $\dot{n}^s_{sw_{i+1}}$ is the remaining molar salt flow on the retantate side and n is the number of stages in the multistage RO process.

Using the volumetric and molar salt flows we can describe the osmotic pressures of the streams leaving mm_i, note that $\dot{V}_{sw_i}$ stream's osmotic pressure is known. The osmotic pressure for the $\dot{V}_{sw_{i+1}}$ stream is $\pi^r_{sw_{i+1}}$ and for the fw stream it is $\pi^r_{fw_i}$, where the superscript 'r' denotesthat this variable is used for the RO stage. Further using Morse osmotic pressure equation with van' tHoff's correction factor [2] and Eqns. (1, 3, 4,), we describe the osmotic pressures as,

$$\dot{V}_{sw_{i+1}} \text{ stream} \quad : \quad \pi^r_{sw_{i+1}} = i\overline{R}T\frac{\dot{n}^s_{sw_{i+1}}}{\dot{V}_{sw_{i+1}}} = i\overline{R}T\frac{\dot{n}^s_{sw_i} - \frac{1}{n}(1-R)\dot{n}^s_{sw_i}}{\dot{V}_{sw_i}(1-X_i)} \tag{5}$$

$$\dot{V}_{fw_i} \text{ stream} \quad : \quad \pi^r_{fw_i} = i\overline{R}T\frac{\dot{n}^s_{fw_i}}{\dot{V}_{fw_i}} = i\overline{R}T\frac{\frac{1}{n}(1-R)\dot{n}^s_{sw_i}}{\dot{V}_{sw_i}X_i} \tag{6}$$

where i is the van't Hoff factor; $\overline{R}$ is the universal gas constant and T is the temperature of the streams, which is constant (rest of the variables are predefined).

With Eqs. (1,3,4,5 and 6) we have all properties associated with the streams entering and leaving the i^{th} membrane module (mm_i) in terms of the known variables. The next step is to express the hydraulic pressure required in mm_i, in terms of X_i and other known streams and membrane properties/variables. For this we use the membrane effectiveness equation. We define the membrane effectiveness equation which was proposed in our previous work[3], to account for the reverse salt flux as

$$\eta_{mm} = \frac{\Delta\pi_{in} - \Delta\pi_{out}}{\Delta\pi_{in} - \Delta P}, \tag{7}$$

where $\Delta\pi_{in}$ is the osmotic pressure difference of the streams entering the membrane module, $\Delta\pi_{out}$ is the difference of the osmotic pressure of the streams exiting the membrane module, and ΔP is the hydraulic pressure difference between the streams entering the membrane module. For a RO process, as there is only one stream entering the membrane module, so that

$$\eta^r_{mm_i} = \frac{\pi^r_{sw_i} - (\pi^r_{sw_{i+1}} - \pi^r_{fw_i})}{\pi^r_{sw_i} - \Delta P^r_i} \tag{8}$$

where $\pi^r_{sw_i}$ is the osmotic pressure of the $\dot{V}_{sw_i}$ stream entering mm_i, π_{fw_i} is the osmotic pressure of the $\dot{V}_{fw_i}$ stream permeating the membrane layer, $\pi_{sw_{i+1}}$ is the osmotic pressure of the saltier retentate stream $\dot{V}_{sw_{i+1}}$ leaving the membrane module, and ΔP^r_i is the difference of hydraulic pressure between the $\dot{V}_{sw_i}$ stream entering mm_i and the $\dot{V}_{fw_i}$ stream leaving the membrane module.

Using the membrane effectiveness Eq. (8) along with Eqs.(5) and (6) we solve for the hydraulic pressure as

$$\Delta P^r_i = (P^r_i - P_0) = \pi_{sw_i} - \frac{\pi_{sw_i} - (\pi_{sw_{i+1}} - \pi_{fw_i})}{\eta^r_{mm}},$$

or with Eqs. (5) and (6)

$$P^r_i = \pi_{sw_i} - \frac{1}{\eta^r_{mm_i}}\left\{\pi_{sw_i} - \left(i\overline{R}T\frac{\dot{n}^s_{sw_i} - \frac{(1-R)\dot{n}^s_{sw_i}}{n}}{\dot{V}_{sw_i}(1-X_i)} - i\overline{R}T\frac{\frac{(1-R)\dot{n}^s_{sw_i}}{n}}{\dot{V}_{sw_i}X_i}\right)\right\} + P_0 \tag{9}$$

The equations suggest that the amount of hydraulic pressure applied in mm_i depends on the membrane's performance properties, osmotic pressure of the $\dot{V}_{sw_i}$ stream entering the membrane module and is ultimately controlled by the desired fw recovery ratio X_i for that particular membrane module mm_i.

2 Multistage Pressure Retarded Osmosis Model

The brine (br) and fresh water (fw) streams enter the PRO part of the OES system at volumetric flows of $\dot{V}_{br}$ and $\dot{V}_{fw}$, respectively; both streams enter at environmental pressure P_0. As the PEX requires equal volumetric flow on each side, the sw stream is split into $\dot{V}''_{sw}$ and $\dot{V}'_{sw,p}$, where $\dot{V}''_{sw}$ is equal to the volumetric flow of the br solution and $\dot{V}'_{sw,p}$ is equal to the volumetric flow of the remainder. $\dot{V}''_{sw}$ stream is pressurized in a pump to match the pressure required in the first membrane module and to overcome the PEX pressure loss δP, before it is sent to the PEX, to exchange pressure between the br stream $\dot{V}_{br_1}$. The presssure of the other $\dot{V}'_{sw,p}$ stream is dropped using a turbine to P_0 bar and is then mixed back with the $\dot{V}''_{sw}$ stream, to make $\dot{V}_{sw}$.

After being pressurized to P_1^p, the brine (br) stream $\dot{V}_{br_1}$ enters the first membrane module (mm_1) on the draw side, along with the fresh water (fw) stream (which is at environemntal presure P_0) on the feed side. The osmotic pressure difference between the streams causes some of the fresh water (fw) from the feed side to cross the membrane layer and dilutes the br stream. The amount of fw water crossing the membrane is controlled by the hydraulic pressure difference ΔP_1^p between the two streams, see Eqs. (18) and (20) further below.

We define a fresh water (fw) mixing ratio Y_i for the i^{th} membrane module (mm_i) which describes how much fw is mixed with the brine (br) stream entering the membrane module. All of the membrane modules have their own separate fw recovery ratio Y_i. The fw recovery ratio for mm_i is defined as

$$Y_i = \frac{\dot{V}_{br_{i+1}}}{\dot{V}_{br_i}} = \frac{\dot{V}_{br_i} + (\dot{V}^p_{fw_i} - \dot{V}^p_{fw_{i+1}})}{\dot{V}_{br_i}} = 1 + \frac{\dot{V}^p_{fw_i}}{\dot{V}_{br_i}} - \frac{\dot{V}^p_{fw_{i+1}}}{\dot{V}_{br_i}} \tag{10}$$

Further we can describe the outgoing brine and fresh water streams in terms of the incoming streams as

$$\dot{V}_{br_{i+1}} = Y_i \dot{V}_{br_i} \tag{11}$$

$$\dot{V}^p_{fw_{i+1}} = \dot{V}^p_{fw_i} - (\dot{V}_{br_{i+1}} - \dot{V}_{br_i}) = \dot{V}^p_{fw_i} - \dot{V}_{br_i}(Y_i - 1) \tag{12}$$

where the brine (br) stream entering the i^{th} membrane module (mm_i) on the draw side is labelled as $\dot{V}_{br_i}$; $\dot{V}^p_{fw_i}$ is the fw stream entering mm_i on the feed side; $\dot{V}_{br_i}$ is the diluted br stream exiting mm_i on the draw side and $\dot{V}^p_{fw_{i+1}}$ is the left over fw stream exiting mm_i on the feed side. The fw mixing ratio for PRO is defined such that Y_i for any PRO membrane is always larger or equal to 1. A Y_i value close to 1 indicates no fw crosses the membrane layer, on the other hand, a higher Y_i value, for instance $Y_i = 2$ would indicate that the amount of fw mixed results in twice the amount of the br stream.

We use the salt rejection coefficient R^p defined for a PRO membrane module to find the salt crossflow from the draw side (br stream) to the feed side (fw stream). The salt rejection coefficient is broadly used in the RO membrane industry, described in Eq. 2. In contrast, the salt rejection coefficient for a membrane module has to be defined. Unlike RO, PRO has two streams entering and leaving the membrane module, hence the rejection cofficient is defined to account for the salt entering the membrane module in both feed and draw streams. The salt rejection coefficient for all membrane modules is kept constant for simulations. It is defined as

$$R^p = \left(1 - \frac{(C_{fw_i} - C_{fw_{i+1}})}{C_{br_i}}\right), \tag{13}$$

where C_{fw_i} is the molar concentration of the fresh water (fw) stream entering the i^{th} membrane module (mm_i); $C_{fw_{i+1}}$ is the concentration of the fw stream exiting mm_i, and C_{br_i} is the molar concentration of the brine (br) stream entering mm_i on the draw side. As we know the molar salt flow in the br and fw stream entering the membrane module, we can find how much salt is left on the draw side (br stream) using the rejection coefficient, as well as, find how much salt is passed on to the feed side (fw stream). In multistage PRO, a membrane module of length L is cut down to n membrane modules of length $\frac{L}{n}$ each. In the same way, we have assumed that the reverse salt flow is distributed among the membrane modules, as the rejection coefficient value used

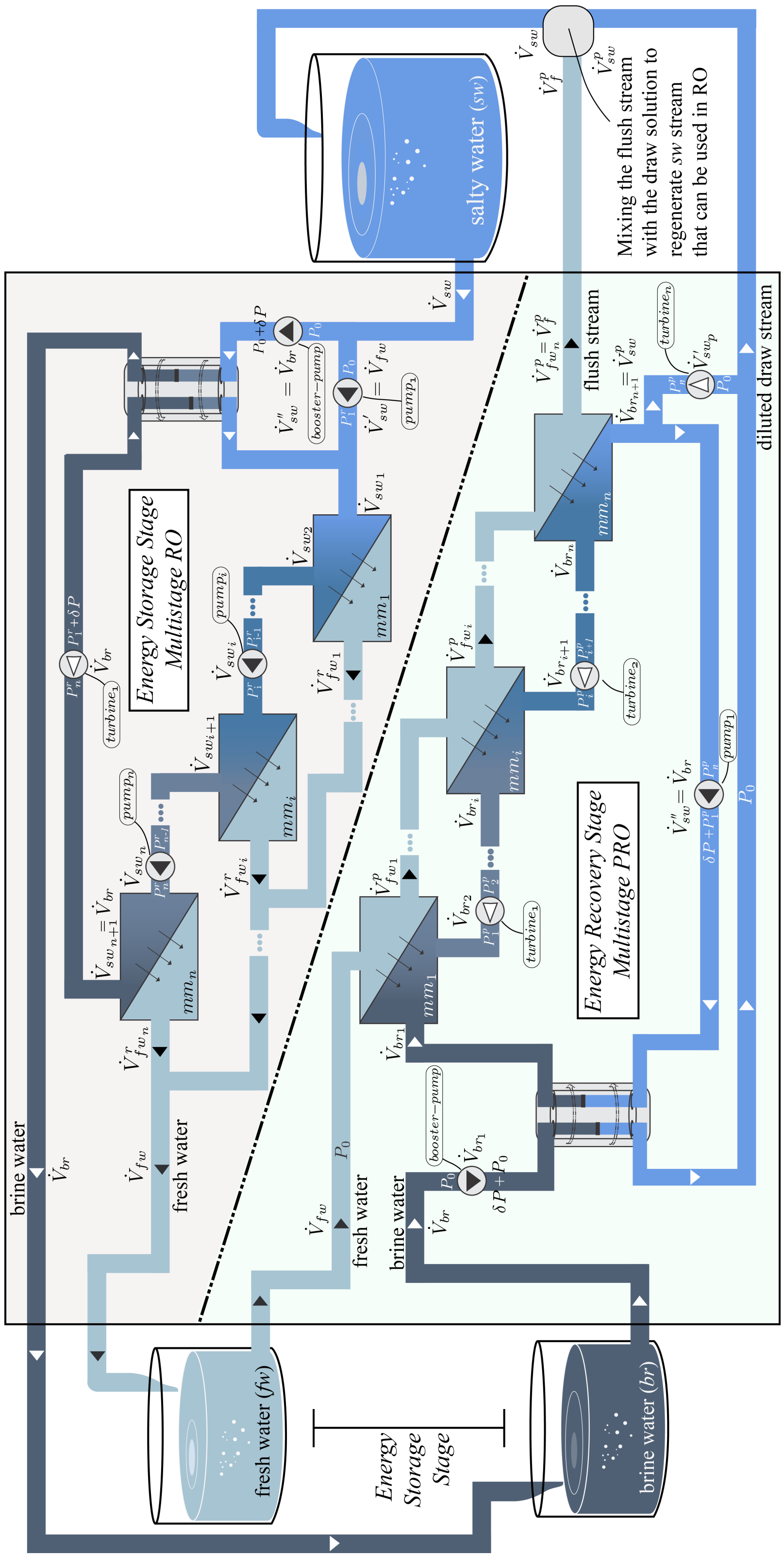

Figure 1: Process schematic of a n-stage OES system. The OES process is inside the box, where the top (light red) section is the energy storage stage when the sw is separated to fw and br, using multistage RO. The bottom (light green) section is the energy recovery stage, where the streams are mixed via multistage PRO.

for simulations are for a full membrane module. The molar salt flow balance for streams leaving mm_i using R^p, Eq. (13) gives

$$\dot{V}_{br_{i+1}} \text{ stream:} \qquad \dot{n}^s_{br_{i+1}} = \dot{n}^s_{br_i} - \frac{(1-R^p)\dot{n}^s_{br_i}}{n}, \tag{14}$$

$$\dot{V}_{fw_{i+1}} \text{ stream:} \qquad \dot{n}^s_{fw_{i+1}} = \dot{n}^s_{fw_i} + (\dot{n}^s_{br_i} - \dot{n}^s_{br_{i+1}}) = \dot{n}^s_{fw_i} + \frac{(1-R^p)\dot{n}^s_{br_i}}{n} \tag{15}$$

where $\dot{n}^s_{br_i}$ is the molar flow of salt in the br stream entering mm_i; $\dot{n}^s_{fw_i}$ is the molar salt flow in the fw stream entering membrane module mm_i; $\dot{n}^s_{br_{i+1}}$ is the remaining molar salt flow on the retantate side; $\dot{n}^s_{fw_{i+1}}$ is the molar salt flow in the fw stream exiting membrane module mm_i on the feed side and n is the number of stages in the multistage PRO process.

Using the volumetric and molar salt flows we describe the osmotic pressures of the streams leaving mm_i, note that the osmotic pressure and other relavent properties of $\dot{V}_{br_i}$ and $\dot{V}_{fw_i}$ streams are known. The osmotic pressure for the $\dot{V}_{br_{i+1}}$ stream is $\pi^p_{br_{i+1}}$ and for the $\dot{V}_{fw_{i+1}}$ it is $\pi^r_{fw_i}$, where the superscript 'p' denotes that this variable is used for the PRO stage. Further using Morse osmotic pressure equation with van't Hoff's correction factor [2] and Eqns. (10, 11, 12, 14, 15), we find the osmotic pressures as

$$V_{br_{i+1}} \text{ stream} \quad : \quad \pi^p_{br_{i+1}} = i\overline{R}T\frac{\dot{n}^p_{br_{i+1}}}{\dot{V}_{br_{i+1}}} = i\overline{R}T\left(\dot{n}^p_{br_i} - \frac{(1-R)\dot{n}^p_{br_i}}{n}\right)\frac{1}{\dot{V}_{br_i}(Y_i)}, \tag{16}$$

$$V_{fw_{i+1}} \text{ stream} \quad : \quad \pi^p_{fw_{i+1}} = i\overline{R}T\frac{\dot{n}^s_{fw_{i+1}}}{\dot{V}_{fw_{i+1}}} = i\overline{R}T\frac{1}{\dot{V}^p_{fw_i} - \dot{V}_{br_i}(Y_i-1)}\left(\dot{n}^s_{fw_i} + \frac{(1-R^p)\dot{n}^s_{br_i}}{n}\right), \tag{17}$$

where i is the van't Hoff factor; $\overline{R}$ is the universal gas constant and T is the temperature of the streams, which is constant (rest of the variables are predefined).

Now we have all properties associated with the streams entering and leaving the i^{th} membrane module (mm_i) in terms of the known variables. The next step is to have the hydraulic pressure required in mm_i, in terms of Y_i and other known streams and membrane properties/variables. For this we use the membrane effectiveness equation and solve for hydraulic pressure. The membrane effectiveness equation for the i^{th} membrane module (mm_i) in the PRO process is defined as

$$\eta^p_{mm_i} = \frac{(\pi^p_{br_i} - \pi^p_{fw_i}) - (\pi^p_{br_{i+1}} - \pi^p_{fw_{i+1}})}{(\pi^p_{br_i} - \pi^p_{fw_i}) - \Delta P^p_i}, \tag{18}$$

where $\pi^p_{br_i}$ is the osmotic pressure of the $\dot{V}_{br_i}$ stream entering the i^{th} membrane module (mm_i) on the draw side; $\pi^p_{br_{i+1}}$ is the osmotic pressure of the $\dot{V}_{br_{i+1}}$ stream, which is exiting (mm_i) on the draw side; π_{fw_i} is the osmotic pressure of the $\dot{V}_{fw_i}$ stream entering mm_i on the feed side; $\pi_{fw_{i+1}}$ is the osmotic pressure of the saltier stream $\dot{V}_{sw_{i+1}}$, which is leaving the membrane module on the feed side. ΔP^p_i is the difference of hydraulic pressure between the draw and the feed streams entering the i^{th} membrane module (mm_i).

We solve Eq. (18) to find the hydraulic pressure

$$\Delta P^p_i = (P^p_i - P_0) = (\pi^p_{br_i} - \pi^p_{fw_i}) - \frac{(\pi^p_{br_i} - \pi^p_{fw_i}) - (\pi^p_{br_{i+1}} - \pi^p_{fw_{i+1}})}{\eta^p_{mm_i}} \tag{19}$$

Further using Eq(s). (16) and (17), we expand the hydraulic pressure for the i^{th} membrane module, in terms of the known variables and the optimizing parameter Y_i, as

$$P^p_i = (\pi^p_{br_i} - \pi^p_{fw_i}) + P_0 - \frac{1}{\eta^p_{mm_i}}\left((\pi^p_{br_i} - \pi^p_{fw_i}) - \left[i\overline{R}T\left(\dot{n}^p_{br_i} - \frac{(1-R^p)\dot{n}^p_{br_i}}{n}\right)\frac{1}{\dot{V}_{br_i}(Y_i)}\right]\right) - \frac{1}{\eta^p_{mm_i}}\left[i\overline{R}T\frac{1}{\dot{V}^p_{fw_i} - \dot{V}_{br_i}(Y_i-1)}\left(\dot{n}^s_{fw_i} + \frac{(1-R^p)\dot{n}^s_{br_i}}{n}\right)\right] \tag{20}$$

The equations suggest that the amount of hydraulic pressure that must be applied to the draw stream entering the i^{th} membrane module (mm_i) depends on the membrane's performance properties, osmotic pressure of the $\dot{V}_{sw_i}$ stream entering the membrane module, but is ultimately controlled by the desired mixing ratio Y_i, for that particular membrane module.

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