**Supporting Information for Integrating Tunable Anion Exchange with
Reverse Osmosis for Enhanced Recovery During Inland Brackish Water
Desalination**

Ryan C. Smith and Arup K. SenGupta*

*Department of Civil and Environmental Engineering, Lehigh University, Bethlehem, PA 18015,
USA*

*Corresponding author, Email: arup.sengupta@lehigh.edu, Tel: (610) 758-3534

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Section S1: Calculation of SI values for varying RO recovery

Given a feedwater concentration, C_F , subjected to reverse osmosis the concentration of the concentrate, C_C , (assuming no loss of ions through the membrane) is given by the equation

$$C_C = \frac{C_F}{1 - R_p} \quad (1)$$

Where R_p is the recovery of the process. **Figure 1** in the text was created by varying the recovery, R_p , from 10% to 90% and calculating the concentration of all ions in the concentrate solution. Then OLI Stream Analyzer Software was used to calculate the activity coefficients, and subsequently scaling potential, for CaSO_4 .

Section S2: Calculation of mixing ratio of ion exchange resins for any feedwater composition

The continued operation of the Hybrid Ion Exchange-Reverse Osmosis (HIX-RO) process relies upon the fact that during the removal step, sulfate is selectively sorbed over chloride and during the regeneration step, chloride is selectively sorbed. During the removal step, sulfate is replaced by chloride by the following reaction

Assuming ideality, the equilibrium constant, K , for an ion exchange reaction is known as the selectivity coefficient, and for the reaction between sulfate and chloride $K_{S/Cl}$ can be calculated by

$$K_{S/Cl} = \frac{y_S x_{Cl}^2 C_T}{x_S y_{Cl}^2 Q} \quad (3)$$

Where x is the fraction of sulfate or chloride in solution, y is the fraction on the resin, C_T is the total equivalent concentration of anions in meq/L, and Q is the resin capacity in meq/g; subscripts S and Cl are sulfate and chloride, respectively. The value of $K_{S/Cl}$, however, does not provide insight as to whether sulfate or chloride is preferred. Instead, the separation factor, $\alpha_{S/Cl}$, does and may be calculated from

$$\alpha_{S/Cl} = \frac{y_S x_{Cl}}{x_S y_{Cl}} \quad (4)$$

When $\alpha_{S/Cl} > 1$, sulfate is the preferred species and vice versa. $\alpha_{S/Cl}$ is significantly different from $K_{S/Cl}$ and is *not* a constant. $\alpha_{S/Cl}$ will vary depending on solution concentration, C_T and resin properties.

For the HIX-RO process, the ion exchange column must be properly designed to ensure that during the forward path of sulfate removal $\alpha_{S/Cl} > 1$ and during the reverse path while using reject as chloride regeneration $\alpha_{S/Cl} < 1$, and this is achieved by mixing together two different resins together in a desired ratio. The individual steps for solving for the proper mixing ratio are as follows:

1. Calculate $\alpha_{S/Cl}$ for both resins at feedwater and RO concentrate concentrations
2. Calculate the overall column separation factor $\alpha_{S/Cl}^*$
3. Determine the range of mixing ratios that ensures $\alpha_{S/Cl}^* > 1$ at feedwater C_T and < 1 at RO concentrate C_T

Step 1: Calculate $\alpha_{S/Cl}$ for both resins at feedwater and RO concentrate concentrations

For a binary system where sulfate and chloride are the only anions present

$$x_S + x_{Cl} = 1 \quad (5)$$

And

$$y_S + y_{Cl} = 1 \quad (6)$$

Equations 5 and 6 are rearranged and substituted into Equation 3 and rearranged to Equation 7 which can be solved for y_S for a given anion exchange resin (known Q and $K_{S/Cl}$ values) and for a specific brackish water and reject stream (known x_S and C_T for both streams).

$$\frac{y_S}{(1 - y_S)^2} = \frac{KQx_S}{(1 - x_S)^2 C_T} \quad (7)$$

Now that both y_S and x_S are known, $\alpha_{S/Cl}$ may be determined as follows

$$\alpha_{S/Cl} = \frac{y_S(1 - x_S)}{x_S(1 - y_S)} \quad (8)$$

Step 2: Calculate the overall column separation factor $\alpha_{S/Cl}^*$

Considering a mixture of two different resins “A” and “B” with masses m_A and m_B , the ratio of resin A, Φ_A , is

$$\Phi_A = \frac{m_A}{m_A + m_B} \quad (9)$$

Similarly for resin B

$$\Phi_B = \frac{m_B}{m_A + m_B} = 1 - \Phi_A \quad (10)$$

The total ion exchange capacity of the column is therefore

$$Q^* = Q_A \Phi_A + Q_B (1 - \Phi_A) \quad (11)$$

And the overall column separation factor $\alpha_{S/Cl}^*$ may be calculated by

$$\alpha_{S/Cl}^* = \frac{y_S^* x_{Cl}}{x_S y_{Cl}^*} \quad (12)$$

Where

$$y_S^* = \frac{y_S^A Q_A \Phi_A + y_S^B Q_B (1 - \Phi_A)}{Q^*} \quad (13)$$

y_S for either resin is determined by solving Eq. 6.

Step 3: Determine the range of mixing ratios that ensures $\alpha_{S/Cl}^* > 1$ at feedwater C_T and < 1 at RO concentrate C_T

The proper mixing ratio is determined by calculating $\alpha_{S/Cl}^*$ as Φ_A is varied from 0 to 1 at both influent and RO concentrate C_T values. The range over which $\alpha_{S/Cl}^* > 1$ at influent C_T and $\alpha_{S/Cl}^* < 1$ at RO concentrate C_T is the range of mixing ratios that will allow the HIX-RO process to operate.

Example with Actual Feedwater

Table S1 gives the composition of agricultural drainage water from the San Joaquin Valley

Table S1. Composition of San Joaquin Valley Agricultural Drainage Water

Ion	meq/L
Na ⁺	50.02
Mg ²⁺	4.99
Ca ²⁺	27.70
Cl ⁻	56.71
SO ₄ ²⁻	21.24
HCO ₃ ⁻	4.77
C_T	82.72

The feedwater can be simplified by assuming all bicarbonate is converted to Cl⁻ through dosing of HCl resulting in a feedwater that has approximately 60 meq/L Cl⁻ and 20 meq/L SO₄²⁻. The properties of polystyrene and polyacrylic resins can be found in open literature and are given in Table S2¹.

Table S2. Properties of polystyrene and polyacrylic resins

	Polystyrene	Polyacrylic
K	35.00	663.4
Q	1.66	1.2

The feedwater C_T is 80 meq/L. If the desalination process is operated at 80% recovery, the C_T of the RO concentrate would be 400 meq/L. From Equations 6 and 7, $\alpha_{S/Cl}$ can be calculated at both C_T values and is given in Table S3.

Table S3. Calculated values of $\alpha_{S/Cl}$ at feedwater and RO concentrate concentrations

	Polystyrene	Polyacrylic
80 meq/L	0.771	4.985
400 meq/L	0.183	1.695

Now, using equations 11 and 12, $\alpha_{S/Cl}^*$ can be calculated over the range of mixing ratios and is shown in Figure S1.

Figure S1. Variation in $\alpha_{S/Cl}^*$ with mixing ratio of polystyrene and polyacrylic resins

The shaded region from ~0.2-0.7 indicates the mixing ratio that will allow high process efficiency.

Table S4. Properties of resins used in this study

Type	Strong Base	Strong Base
Matrix	Polystyrene	Polyacrylic
Functional Group	Quaternary Amine	Quaternary Amine
Structure

Figure S2. Controlling $\alpha_{S/Cl}$ by changing the either the matrix or functional group of the resin

Section S3: Characterization of RO system

Flux and flow rates for each cycle are given for the 50/50 polyacrylic/polystyrene run, **Table S5**, and the pure polystyrene, **Table S6**. The Dow Filmtec SW30-2540 RO membrane has an effective membrane area of 2.8 m².

Table S5. RO data for 50/50 polyacrylic/polystyrene run

Cycle	Permeate Flux (L/m ² -hr)	Permeate Flow Rate (L/min)	Concentrate Flow Rate (L/min)	Total Flow Rate (L/min)	Percent Recovery
1	46.0	2.15	0.59	2.74	78.5%
2	43.6	2.03	0.44	2.48	82.1%
3	46.7	2.18	0.56	2.74	79.7%
4	44.7	2.09	0.58	2.66	78.4%
5	42.1	1.96	0.57	2.54	77.5%
6	44.4	2.07	0.56	2.63	78.8%
7	41.7	1.95	0.60	2.55	76.4%
8	42.7	2.00	0.64	2.63	75.8%
9	44.5	2.08	0.51	2.59	80.2%
10	40.4	1.88	0.48	2.36	79.7%

Table S6. RO data for pure polystyrene run

Cycle	Permeate Flux (L/m ² -hr)	Permeate Flow Rate (L/min)	Concentrate Flow Rate (L/min)	Total Flow Rate (L/min)	Percent Recovery
1	39.1	1.82	0.41	2.24	81.6%
2	38.1	1.78	0.45	2.23	79.8%
3	35.3	1.65	0.38	2.02	81.4%
4	36.9	1.72	0.45	2.17	79.2%
5	36.6	1.71	0.42	2.13	80.3%
6	33.1	1.54	0.33	1.87	82.4%
7	35.8	1.67	0.43	2.10	79.5%
8	37.1	1.73	0.45	2.18	79.3%
9	33.4	1.56	0.35	1.91	81.7%
10	32.7	1.53	0.39	1.92	79.5%

Figure S3. Setup for Reverse Osmosis

Figure S4. (A) Sulfate mass balance for mixed bed system (B) Sulfate mass balance for polystyrene bed

Figure S5. Breakthrough curve for 50/50 polystyrene/polyacrylic column

Section S4: In-column precipitation procedure

The procedure for studying the potential for in-column precipitation is detailed in **Figure S6**.

Figure S6. Procedure for measuring potential for precipitation of CaSO₄ in the ion exchange column

To begin, the ion exchange column is placed in chloride form by passing a dilute NaCl solution until the column is completely in Cl⁻ form. The column is then washed with DI water until no chloride is detected in the effluent. The influent solution is the same as the feedwater except all bicarbonate is replaced by chloride. Then, like the large scale system, 20 BVs of solution are passed and collected. Synthetic regenerant is used that is 5 times the concentration of the feedwater but all the sulfate has been replaced by chloride. 4BV of regenerant is then passed upflow through the column and collected in a fractional collector.

REFERENCES

(1) Clifford, D.; Weber Jr., W.J. The determinants of divalent/monovalent selectivity in anion exchangers. *React. Polym.* **1983**, *1*, 77-89.