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Prospects and challenges for high-pressure reverse osmosis

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Deriving the minimum energy for separation calculation

To calculate the energy efficiency of an RO process, we first calculate the minimum energy for separation (the thermodynamic limit) by integrating the following equation,

$$dG = RT\, ln(a_w) dn_w \tag{S1}$$

in which dG is the differential Gibbs free energy for removing dn_w moles of water from a saline solution, a_w is the water activity coefficient, T is absolute temperature, and R is the ideal gas constant[18]. Given an appropriate activity coefficient model[20-21], this equation can be solved analytically, and one simplifying assumption commonly used is to treat the salt solution as a NaCl solution of equal concentration, which leads to minimal errors in calculating osmotic pressures for NaCl-rich salt solutions such as seawater[22] and formation water[16]. Because produced waters[3] and FGD wastewater[2] would have similar NaCl fractions after divalent cation removal during pretreatment (to avoid membrane scaling[23]), we expect that this simplifying assumption will also allow us to accurately determine the osmotic pressure for these brines. To further simplify our calculations, we used an empirical equation[24-25] (rather than an activity coefficient model) for calculating the osmotic pressure of an NaCl solution as a function of salt concentration:

$$\pi = (40.714\frac{atm}{M})\, c + (6.2917\frac{atm}{M^2})\, c^2 \tag{S2}$$

where c is molar concentration and π is the osmotic pressure in atm[24-25]. Using this equation, we calculate the thermodynamic limit for RO separation as the pressure-volume work[26-27] needed to force a volume of water V through the membrane against an osmotic pressure π using a reversible piston:

$$E = \frac{1}{V_f}\int_0^{V_f} \pi(V)dV = \frac{1}{r_f}\int_0^{r_f} \pi(r)dr \tag{S3}$$

where V is the volume of water that permeates through the membrane, r is the recovery ratio (permeate volume divided by feed volume), the subscript f denotes the final conditions, and E is the energy required per unit feed volume[26]. Using a substitution of variables and boundary conditions to convert from recovery ratio to concentration

$$r = 1 - c_0/c \tag{S4}$$

$$dr = \frac{c_0}{c^2}dc \tag{S5}$$

$$At\, r = 0, c = c_0 \tag{S6}$$

$$At\, r = r_f, c = \frac{c_0}{1 - r_f} = c_f \tag{S7}$$

we can integrate to obtain an analytical expression for the thermodynamic limit as a function of salt concentration:

$$E = \frac{1}{1 - c_f/c_0}\int_{c_0}^{c_f} \pi(c)\frac{c_0}{c^2}dc = \frac{c_f c_0}{c_f - c_0}[40.714\frac{atm}{M}\ln\left(\frac{c_f}{c_0}\right) + 6.2971\frac{atm}{M^2}(c_f - c_0)] \tag{S8}$$

Chemical softening reactions

To prevent scaling, about 99% of the divalent cations must be removed during pretreatment[8], and quicklime (CaO) and soda ash (Na_2CO_3) are the compounds used to remove carbonate and noncarbonate hardness respectively[23, 35]. CaO precipitates CO_2, HCO_3^-, Mg^{2+}, and Ca^{2+} as carbonates and hydroxides at pH 9.3-10.5[23]

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3(ppt) + H_2O \tag{S9}$$

$$Ca^{2+} + Ca(OH)_2 + 2\,HCO_3^- \rightarrow 2\,CaCO_3(ppt) + 2\,H_2O \tag{S10}$$

$$Mg^{2+} + 2\,Ca(OH)_2 + 2\,HCO_3^- \rightarrow 2\,CaCO_3(ppt) + Mg(OH)_2(ppt) + 2\,H_2O \tag{S11}$$

$$Mg^{2+} + Ca(OH)_2 + SO_4^{2-} \rightarrow Mg(OH)_2(ppt) + Ca^{2+} + SO_4^{2-} \tag{S12}$$

Soda ash removes the remaining divalent cations via the reaction[25]:

$$Ca^{2+} + SO_4^{2-} + Na_2CO_3 \rightarrow CaCO_3(ppt) + SO_4^{2-} + 2\,Na^+ \tag{S13}$$

To determine the amount of each chemical needed, we first convert the relevant ions (most divalent cations, HCO_3^-, and CO_2) to an equivalent concentration of $CaCO_3$.

$$C_{CaCO_3} = C_i \frac{MW_{CaCO_3}}{MW_i} \tag{S14}$$

Next, we compare the $CaCO_3$ equivalent concentrations of Ca^{2+}, Mg^{2+}, and HCO_3^- to determine the amount of calcium and magnesium hardness that will precipitate via reactions involving bicarbonate salts. The calcium precipitates preferentially, followed by magnesium and other cations if sufficient bicarbonate is present. We then calculate the lime required to precipitate the carbonate hardness (CO_2 + bicarbonate salt reactions) and the soda ash required to precipitate the noncarbonate hardness (the remaining salts).

$$C_{CaO} = \left[C_{CaCO_3}(from\ CO_2) + C_{CaCO_3}(from\ bicarbonates +\ hydroxides)\right]\frac{MW_{CaO}}{MW_{CaCO_3}} \tag{S15}$$

$$C_{Na_2CO_3} = \left[C_{CaCO_3}(from\ remaining\ divalent\ cations)\right]\frac{MW_{Na_2CO_3}}{MW_{CaCO_3}} \tag{S16}$$