Supporting information

Theoretical uphill transport

To demonstrate the effect of uphill transport of multivalent ions on the voltage in RED, this supporting information will further elaborate on this uphill transport. Considering a case without net charge transport (i.e. open circuit) and a infinite large residence time of the feed water (i.e. batch mode), the transport of multivalent Mg^{2+} ions through a CEM, in exchange for monovalent Na^+ ions, can be calculated from:

$$\left(\frac{\gamma_{Na^+,s}\cdot\left(c_{Na^+,s}-2J/V_s\right)}{\gamma_{Na^+,r}\cdot\left(c_{Na^+,r}+2J/V_r\right)}\right)=\left(\frac{\gamma_{Mg^{2+},s}\cdot\left(c_{Mg^{2+},s}+J/V_s\right)}{\gamma_{Mg^{2+},r}\cdot\left(c_{Mg^{2+},r}-J/V_r\right)}\right)^{1/2} \qquad \text{(eq. S1)}$$

In which γ is the activity coefficient (-) for Na^+ or Mg^{2+}, c is the (initial) concentration in the feed water (M), J is the molar transport of Mg^{2+} from the river water compartment towards the seawater compartment (mol), V is the volume of the compartments (L) and the subscripts s and r indicate seawater or river water, respectively. A similar equation can be derived for the transport of multivalent SO_4^{2-} ions through the AEM, in exchange for monovalent Cl^-.

Assuming that the compartments for seawater and river water are equal in volume (i.e., $V_s = V_r = V$), the molar transport per volume of compartment, J/V, can be calculated. This molar transport is shown in Fig. S1 as a function of the fraction of $MgSO_4$ in the seawater feed, river water feed, or both feeds. The corresponding concentrations of NaCl and $MgSO_4$ in the river water compartment, before and after this uphill transport of $MgSO_4$, are given in Fig. S2.

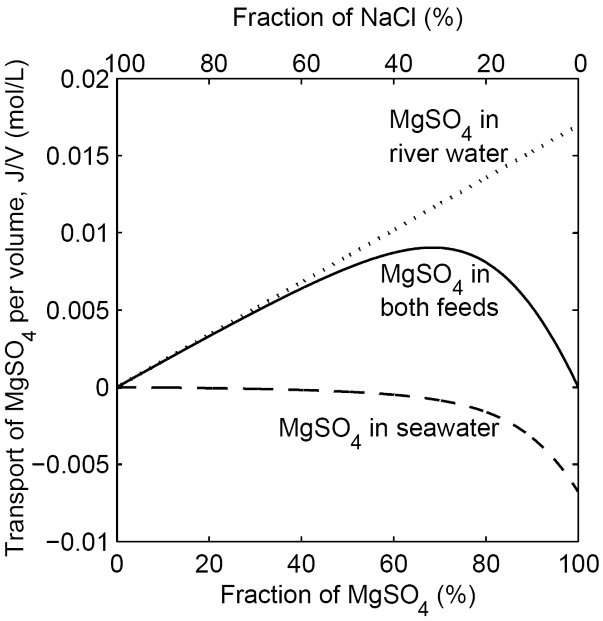

Figure S1: Molar transport of $MgSO_4$ per volume (i.e., J/V) as a function of the fraction of $MgSO_4$ in the seawater feed, river water feed, or both feeds. Positive values indicate transport from the river water compartment towards the seawater compartment, while negative values correspond to transport in opposite direction.

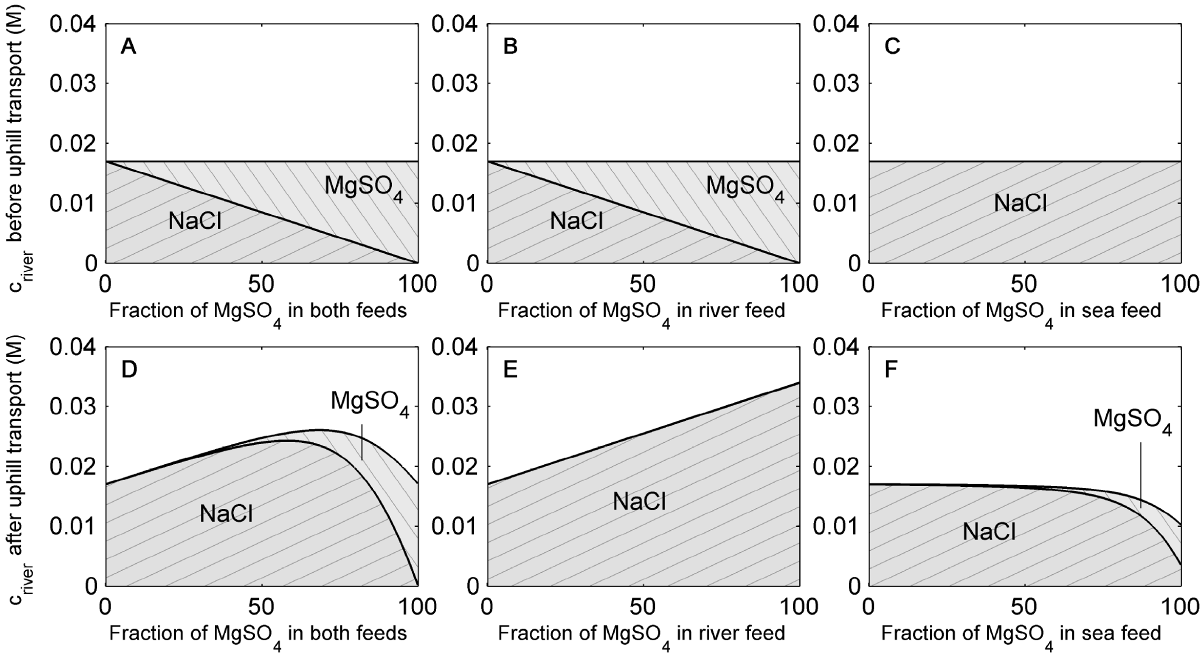

Figure S2: The concentrations of NaCl and $MgSO_4$ in the river water compartment, before uphill transport (A, B and C) and after uphill transport of $MgSO_4$ (D, E, F). The left panels (A and D) show the case with $MgSO_4$ initially present in both feeds, the middle panels (D and E) show the case with $MgSO_4$ initially present in the river water feed only, while the right panels (C and F) show the case with $MgSO_4$ initially present in the seawater feed only.

The most practical case, in which $MgSO_4$ is present in both the seawater and river water feed, shows a maximum transport at a fraction of $MgSO_4$ of approximately 70% (Fig. S1). This maximum does not correspond to a 50-50% mixture, for several reasons. First of all, the membrane voltage is dependent on the logarithm of the ratio in concentrations (eq. S1), which disables a linear relation between fraction of $MgSO_4$ in the feed water and its transport. Furthermore, the transport of monovalent ions is twice that of the multivalent ions. Thirdly, the activity coefficients for NaCl are different than that for $MgSO_4$. The combination of these effects results in a maximum uphill transport at a fraction of $MgSO_4$ of approximately 70%.

As a result of the uphill transport of $MgSO_4$, the concentration of NaCl increases in the river water compartment (Fig. S2A and S2D), most pronounced for mixtures with initial $MgSO_4$ fractions close to 70%. Consequently, the ratio in NaCl concentrations over each membrane is reduced, which lowers the voltage according to the Nernst equation.

The transport of $MgSO_4$ is most significant for the case when $MgSO_4$ is only present in the river water feed (Fig. S1). In this case, additional transport of $MgSO_4$ is required from the river water compartment towards the seawater compartment, as $MgSO_4$ is initially absent in the seawater feed. To restore the concentration gradient in $MgSO_4$ as obeyed in eq. S1, almost all $MgSO_4$ initially available in the river water compartment is transported to the seawater compartment, as demonstrated in Fig. S2B and S2E, and the nearly linear line in Fig. S1. To compensate the charge transport of the multivalent ions, NaCl is transported from the seawater compartment to the river water compartment, which increases the concentration of NaCl in the river water compartment (Fig. S2E) and reduces the obtained voltage.

Fig. S1 furthermore shows that the transport of $MgSO_4$ is smallest for the case when $MgSO_4$ is only present in the seawater in fractions < 80%. Due to the absence of $MgSO_4$ in the river water, the ratio in $MgSO_4$ concentrations over each membrane is already high (in fact, infinitely high, due to a zero concentration in the river water) in the initial feed concentrations. Hence, no uphill transport is required, and $MgSO_4$ is even transported in

small quantities to from the seawater to the river water. Only for fractions of $MgSO_4 > 80\%$, $MgSO_4$ is significantly transported in this direction, which is also deduced from the concentrations in Fig. S2F.
Considering these three cases, the large differences in the final river water concentrations and hence in the obtained voltages show the major impact of (uphill) transport of multivalent ions in exchange for monovalent ions. This difference is highlighted comparing the cases with $MgSO_4$ in both feeds and $MgSO_4$ in the seawater feed only. While the initial concentrations in the seawater feed are equal in these cases, the presence of $MgSO_4$ in the river water feed generates a substantial ion exchange in one of these cases. In the other case, where $MgSO_4$ is only fed to the seawater, the (uphill) transport of $MgSO_4$ is negligible for fractions < 80%. The large difference in the final concentrations of NaCl and $MgSO_4$ of these two cases and hence the obtained voltage exemplifies the significant effect of uphill transport.

EDX measurements

The EDX analysis (JEOL, JSM 6010LA, United States) was performed over at least two cross-sectional lines of each sample, each line comprising at least 10 scan points. An exemplary SEM-image with the corresponding position of two EDX series is given in Fig. S3.

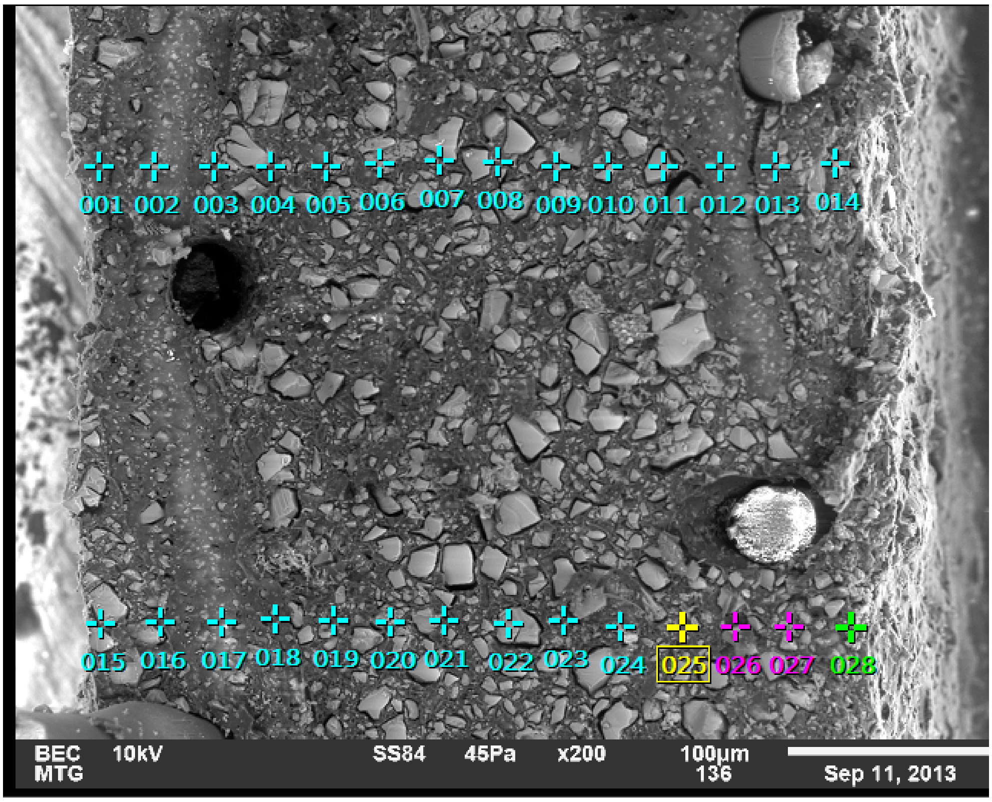

Figure S3: SEM-image of Ralex cation exchange membrane, with corresponding position of two EDX series, each comprising 14 data points, as indicated by the numbered crosses.

For each data point, an EDX analysis (10 kV, spotsize 80 - 84) was performed for 60 seconds. The spectra were analyzed for the elements Na, Cl, Mg, S and Au. The fraction of Au originates from the coating of the SEM-holders and is not of interest for this research. However, this element was included in the spectrum analysis to better distinguish the contribution of S-atoms, whose spectrum is close to that of Au. The total number of counts for each point was typically approximately 200000 - 500000. For the Ralex and Fujifilm CEMs, typically 20 - 80% of the detected atoms are Na and Mg. For Neosepta membranes, these cations contribute less to the total detected atoms (typically 10 – 50%), because the reinforcement of this membrane comprises Cl-atoms, which contribute additionally to the acquired counts in the EDX measurement. Because the exact number of counts is dependent on the local sample angle, material and the spotsize, the EDX analysis can only be used for deducing relative concentrations of the detected elements (e.g., Na and Mg) and cannot infer absolute concentrations of these atoms.

Effluent concentrations

The salinity ratios of each ionic species (Na^+, Cl^-, Mg^{2+}, SO_4^{2-}) in the effluent feed water, for stacks with Ralex and Fujifilm membranes, are demonstrated in Fig. S3.

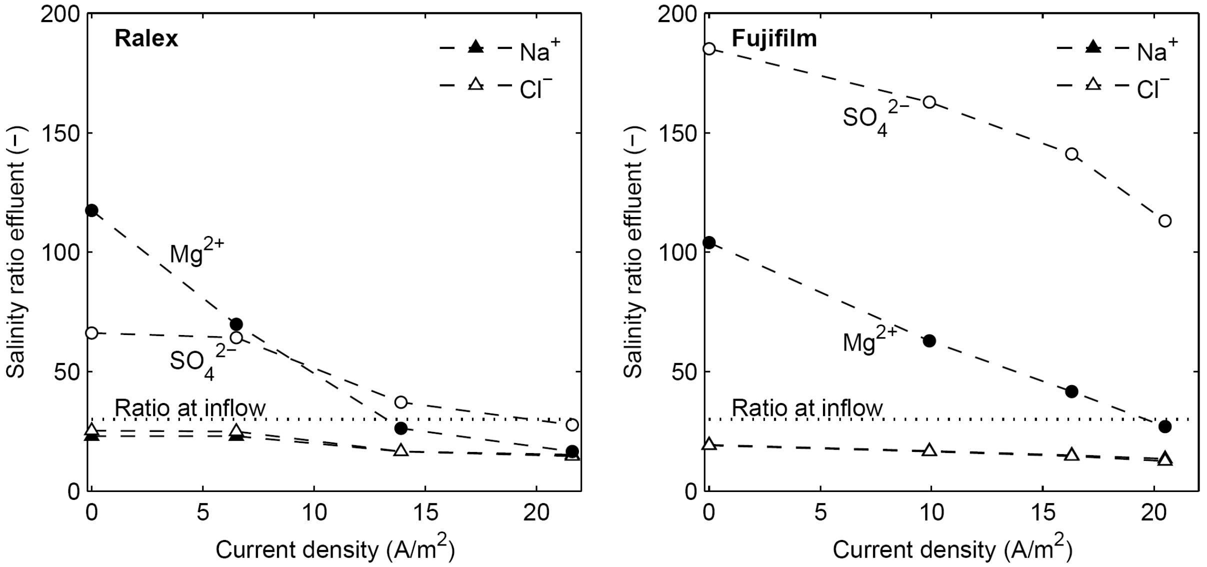

Figure S4: Ratio between seawater and river water effluent for each ionic species (Na^+*,* Cl^-*,* Mg^{2+}*,* SO_4^{2-}*), for stacks with Ralex (left) and Fujifilm membranes (right).*

Fig. S3 shows the same trends for the stacks with Ralex and Fujifilm membranes compared to the stack with Neosepta membranes (Fig. 6). Comparing the different membrane types in more detail, the transport of Na^+, Cl^- and Mg^{2+} is similar for all membrane types, while the transport of the SO_4^{2-} is significantly higher in Fujifilm membranes, followed by Neosepta and Ralex membranes. The differences in transport rate of SO_4^{2-} are due to the differences in membrane resistance. A lower membrane resistance corresponds to more uphill transport, as indicated earlier by the electrical circuit (Fig. 1C). The differences in membrane resistance are more pronounced for the AEMs than for the CEMs, and therefore the differences in the concentration ratios are more significant for SO_4^{2-} than for Mg^{2+}.