

**Multi-physical modeling of reverse electrodialysis**

Energy extraction from salinity gradients (salinity gradient Power, SG<sub>P</sub>) represents a novel and valuable renewable energy source. Among the existing SG<sub>P</sub> technologies, reverse electrodialysis (RED) is the oldest and one of the most promising. RED is a membrane-based electrochemical process that directly converts the salinity gradient energy into electric current. More precisely, in a RED unit two solutions at different concentration flow in two series of alternating channels, which are formed by placing two alternated series of cation and anion exchange membranes (CEMs) and AEMs, respectively). The chemical potential difference between the two solutions generates an electric potential difference over each membrane along with a selective transpot of cations (across CEMs) and anions (across AEMs) from each concentrate channel towards the two dilute ones. Eventually, the so generated ionic current is converted by redox reactions into an electric current in the two electrode compartments closing the stack.

RED is characterized by a number of different physical phenomena, which should be properly modeled in order to drive the process design and optimization. In this regard, this work presents a novel approach for multi-physical modeling of the entire RED process. A single 2-D cell pair (encompassing two membranes and two feed channels) is the identified process repeating unit, coinciding with the computational domain investigated. In order to fully cover the phenomena complexity of the operation of a RED unit, a number of different physical models were implemented and interconnected each other. In particular: (i) Navier-Stokes and continuity equations were solved for fluid dynamics modeling; (ii) Nernst-Planck equation was used for ion mass transfer; (iii) local electroneutrality condition was assumed everywhere, taking also into account the fixed charges concentration within the membranes. At membrane-solution interfaces: (iv) Donnan theory was applied to simulate voltage jump; (v) partition coefficients were adopted to simulate concentration jump. Finally, the model is completed by (vi) algebraic equations for the calculation of stack potential, current density and gross / net power density in a stack of any given number of cell pairs, by taking into account also the electrode compartments resistance and the overall domain were obtained, and the values of gross and net power density were computed.

As model outputs, the distributions of velocity, pressure, concentrations, fluxes and potential in the overall domain were obtained, and the values of gross and net power density were computed.

Keywords: Reverse electrodialysis, Multi-physics, Finite elements, Profiled membranes, Spacers.



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### **Long-run operation of a reverse electrodialysis system fed with wastewater solutions**

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In the framework of salinity gradient power technologies, reverse electrodialysis (RED) is one of the most promising. In RED, two solutions of different salt concentration are fed into a series of alternate compartments, the one fed by the low salinity solution, the other by the high salinity solution. Compartments are separated by anion and cation exchange membranes alternatively piled to form a stack. Selective ion transport from the concentrate compartment to the dilute one across the membranes allows to generate an ionic current, which is eventually converted into electric current by means of suitable electrode compartments closing the stack.

Several options for the feed solutions are possible. Natural waters were first considered as a potential source of salinity gradient, such as: river water and seawater or concentrated brines and low-salinity waters. Another alternative is the use of artificial solutions as feed solutions within closed-loop systems in which deployed salinity gradient of solutions exiting the RED unit is then regenerated by means of a regeneration step (e.g.: using low-grade heat, in RED heat engines; or , using electricity, in RED batteries).

A nascent, still less explored alternative is the use of different industrial wastewaters as feed solutions. In fact, in several different scenarios, waste streams to be disposed can actually represent a very effective source of salinity gradient to be exploited before the natural mixing with the receiving water body occurs.

In the present work a high salinity waste brine from a fish processing factory and a low-salinity water from a civil wastewater Membrane Bio Reactor (MBR) treatment plant were selected as feed solutions for an extensive investigation on a laboratory-scale RED unit (10 cell-pairs with a 10 cm × 10 cm active membrane area). Firstly, the RED unit performance was characterized with artificial NaCl solutions prepared with the same NaCl concentration as the real streams, in order to have a comparison-reference for tests with real solutions. Subsequently, long-run tests with real feed solutions were performed (firstly feeding real brine and artificial low-salinity feed, then artificial brine and real low-salinity feed and, finally, feeding the stack with both real feed), operating the RED unit in an uninterrupted way for more than 2 weeks for each case. The time-evolution of system performance parameters (pressure drops, stack resistance, power output, etc.) was registered and analyzed in order to assess the relevant effect of the real feed solutions, likely related to fouling/scaling/plugging phenomena in the lab-stack. Also counter washing and chemical washing procedures were periodically (typically, once per week) implemented in order to highlight their effectiveness in restoring process performance. On overall, results collected over a period