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Exergy as a Useful Variable for Quickly Assessing the Theoretical Maximum Power of Salinity Gradient Energy Systems

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Abstract: It is known that mechanical work, and in turn electricity, can be produced from a difference in the chemical potential that may result from a salinity gradient. Such a gradient may be found, for instance, in an estuary where a stream of soft water is flooding into a sink of salty water which we may find in an ocean, gulf or salt lake. Various technological approaches are proposed for the production of energy from a salinity gradient between a stream of soft water and a source of salty water. Before considering the implementation of a typical technology, it is of utmost importance to be able to compare various technological approaches, on the same basis, using the appropriate variables and mathematical formulations. In this context, exergy balance can become a very useful tool for an easy and quick evaluation of the maximum thermodynamic work that can be produced from energy systems. In this short paper, we briefly introduce the use of exergy for enabling us to easily and quickly assess the theoretical maximum power or ideal reversible work we may expect from typical salinity gradient energy systems.

Keywords: exergy; salinity gradient energy systems; electric power

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1. Introduction

It is known that mechanical work, and in turn electricity, can be produced from a difference in the chemical potential that may result from a salinity gradient. Such a gradient may be found, for instance, in an estuary where a stream of soft water is flooding into a sink of salty water that we may find in an ocean, gulf or salt lake. Various technological approaches, still under development, are proposed for the production of electric power out of a salinity gradient between a stream of soft water and a source of

salty water. One of the technologies being intensively studied and experimented is called Pressure Retarded Osmosis (PRO). This technology relies on the use of water permeable membranes to pressurize a stream of salt water by osmotic permeation of water through the membranes, enabling this pressurized stream to be used for the production of mechanical work through the use of a hydraulic turbine (see references [1-10]). Another technology that is examined is called Reversed ElectroDialysis (RED), which relies on salt ionic diffusion from a concentrated stream to a dilute stream, through the use of selective ionic membranes [11-14]. The transport of ions through the ionic membranes allows the production of a continuous current (DC) at a given voltage, thus an electrical power. Other technological approaches have been proposed or experimented [15,16], but it is beyond the scope of this paper to present and describe all the technological approaches proposed for the production of energy from salinity gradients.

Before considering implementation of a technology for a specific application related to power production from salinity gradients, it is of utmost importance to be able to compare the various technological approaches that are proposed. Such comparisons must be done on a common basis, using the appropriate variables and mathematical formulations. In this context, exergy balance could be a very useful tool for an easy and quick evaluation of the maximum thermodynamic mechanical power that can be produced from such energy systems. The scope of this paper is to briefly introduce the use of exergy for enabling us to easily and quickly calculate the maximum theoretical power we may expect from typical salinity gradient energy systems, in the perspective of simple thermodynamic. This will be illustrated with cases corresponding to ideal, reversible processes. Topics related to irreversibility for real systems are beyond the scope of this introductory article.

2. Defining the System

We start with the principle that it is possible to calculate the maximum power that can be produced out of a salinity gradient between two streams of different salinities. As shown in Figure 1, let us consider an open system, represented by a box, with two inlet streams of different salinities, namely streams A and B. Each of these streams is considered as composed of water (solvent) containing a dissolved solute (salt). In Figure 1, the dashed line indicates a separation or barrier between two types of compartments, each of them respectively linked to stream A and stream B. Inside the box, we consider that there is a mass exchange between the two types of compartments, such that at the outlet of the system, there are two streams, respectively A' and B'. Mass exchange is considered as two internal streams as shown in Figure 1: one describing salt transport (salt) and another defining transport of water (w).

In a system based on membrane water permeation such as PRO, the desired phenomena is osmotic transport of water from a dilute type of compartment fed by a diluted stream (stream B), to a concentrate type one fed by a concentrated stream (stream A). In the case of a technology such as RED, the desired phenomenon is ionic transport of salt from the concentrate type of compartment to the diluted type one.
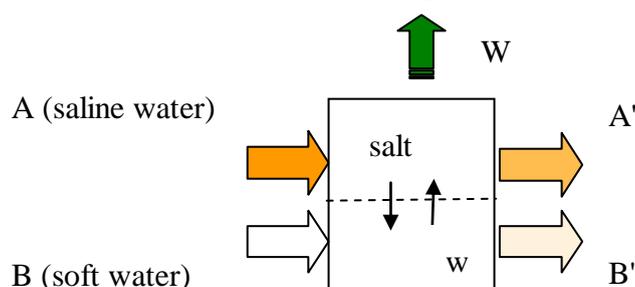
In order to calculate thermodynamically the maximum power W that could be produced from a system as presented in Figure 1, we must first specify each of the following:

(i) Pressure and temperature for each of streams A, A', B and B'

(ii) Mass flowrate and composition of each of the inlet streams A and B

(iii) Mass flowrate and direction of each of the internal stream describing respectively transport of water and transport of salt.

2. Assessing Mass Balance

The mass balance presented by Equations 1 to 4 enables us to calculate composition and flow rate, of each of the outlet streams A' and B'. The salt mass balance is described by Equations 1 and 2, while the water mass balance is described by Equations 3 and 4:

$$F_A x_A - \tau_S F_A x_A = F_{A'} x_{A'} \tag{1}$$

$$F_B x_B + \tau_S F_A x_A = F_{B'} x_{B'} \tag{2}$$

$$F_A (1 - x_A) + \tau_w F_B (1 - x_B) = F_{A'} (1 - x_{A'}) \tag{3}$$

$$F_B (1 - x_B) - \tau_w F_B (1 - x_B) = F_{B'} (1 - x_{B'}) \tag{4}$$

where F refers to mass flowrate (kg/s) of a specific stream, x is the mass fraction of salt in a specific stream, τ_s is the fraction of salt in stream A transferred to steam B', and τ_w is the fraction of water in stream B transferred to stream A'. For fixed or known values of τ_s, τ_w, F_A, F_B, x_A and x_B, composition and flow of each of the exit streams A' and B' can then be calculated.

3. Assessing the Exergy Balance

With the mass balance values, we can then calculate the theoretical thermodynamic power resulting from the internal exchange of matter of the system, without any consideration of the design of the energy system, using a simple exergy balance. The thermodynamic power of a system as presented in Figure 1 can be easily calculated by Equation 5:

$$W = E_{in} - E_{out} \tag{5}$$

Where E_{in} is the total inlet exergy flow (J/s) and E_{out} is the total outlet exergy flow. Starting from known value of specific exergy for each of the four streams A, A', B and B', Equation 5 becomes:

$$W = (F_A e_A + F_B e_B) - (F_{A'} e_{A'} + F_{B'} e_{B'})$$ (6)

Where F is the mass flow rate (kg/s) of a specific stream and e is to the specific exergy (J/kg) of a given stream.

Exergy is a thermodynamic state variable introduced as a measure of the capability of a stream to produce useful work [17]. It is the maximum work that can be produced when this stream is at equilibrium with a reference environment. Since we deal with streams characterized by their temperature, pressure and salinity, a reference state for liquid streams could stand for a stream of pure water (salinity zero) at a reference temperature of 0 ℃ and atmospheric pressure (1 atm) with the reference state for salt being an infinitely dissolved solution. For a system where kinetic and gravitational energy are to be accounted, the reference state could also include a reference height of zero and a stream velocity of zero. At reference conditions, specific exergy of a stream is zero.

Total mechanical specific exergy (relative to a reference state) of a given stream can be calculated from Equation 7:

$$e = e_t + e_k + e_z + e_{ch}$$ (7)

where e_t is the specific thermomechanical exergy, e_{kt} is the specific kinetic exergy (equal to specific kinetic energy), e_z is specific gravitational exergy (equal to specific gravitational potential energy) and e_{ch} is the chemical exergy. For saline solutions for which thermodynamic properties such as enthalpy and entropy are known, Equation 8 can be used, where h is the specific enthalpy of the stream (J/kg), s is the specific entropy of the stream (J/kg-K), T_0 is the reference absolute temperature (ex: 273 K), with h_0 and s_0 as enthalpy and entropy of the reference state respectively. Kinetic and gravitational exergies are to be calculated with Equations 9 and 10 respectively, where v is the velocity of the fluid (m/s), and Z is a given height (m) and g is the gravitation constant (9.807 m/s^2):

$$e_t + e_{ch} = (h - h_0) - T_0(s - s_0)$$ (8)

$$e_k = (\frac{1}{2} v^2)$$ (9)

$$e_Z = Zg$$ (10)

In the case of a membrane system involving a low fluid velocity (ex: below 1 m/s), kinetic exergy can be neglected, and where height is of no concern or of low value (ex: below 1 m), potential exergy is to be neglected also. Total exergy of a stream can then simply be calculated from Equation 8.

Setting h_0 and s_0 to zero, Equation 8 reduces to Equation 11

$$e_{t,j} + e_{ch,j} = h_j - T_0 s_j$$ (11)

where subscript j refers to a specific stream i.e., A, B, A' or B'. According to this equation, we only need h_i and s_i to calculate the specific exergy of a stream j, each of these variables being function of temperature, pressure and composition of the stream. For the general case of non-ideal mixture such as concentrated brines, values of specific enthalpy and specific entropy of a stream can be obtained from

the literature (tables, empirical equations, etc.), or one may use commercial software. Many commercial process simulators are well equipped with activity coefficient models allowing the calculation of thermodynamic properties such as enthalpy and entropy of electrolytes. Equation 11 can then straightforwardly be applied to obtain the thermomechanical and chemical exergy of a stream.

4. Examples

4.1. Presentation of the examples and methodology

Based on the methodology described above, we can easily figure out the maximum mechanical work (and then electricity) that can be produced from a difference in the chemical potential that may result from a salinity gradient between a stream of soft water (stream B in Figure 1) and a stream of salty water (stream A in Figure 1). Three situations (case studies) describing open systems are briefly examined here. The parameters used for calculations are presented in Table 1. One case refers to a general system involving the mixing of 1,000 kg/s of soft water with a infinite sink of oceanic water, another one refers to a device involving water transport through a physical barrier (semi-permeable membrane) such as a PRO type system, and the last case refers to a system involving salt transport (through a set of ionic membranes) such as a RED type system. For each of the three cases, temperature is fixed at 10 ℃ and pressure at 1 atm. It should be emphasized here that the cases correspond to ideal reversible processes, not real ones.

For a simple an easy evaluation of h and s (relative to values at reference state set to zero) of oceanic saline water, and for the purpose of the calculations related to the case studies presented here, we use the following equations proposed by Millero *et al.* [18]):

$$h = A_H \xi + B_H \xi^{3/2} + C_H \xi^2 \tag{12}$$

$$A_H = 3.4086 \times 10^{-3} - 6.3798 \times 10^{-5}\theta + 1.3877 \times 10^{-6}\theta^2 - 1.0512 \times 10^{-8}\theta^3 \tag{12a}$$

$$B_H = 7.9350 \times 10^{-4} + 1.0760 \times 10^{-4}\theta - 6.3923 \times 10^{-7}\theta^2 + 8.60 \times 10^{-9}\theta^3 \tag{12b}$$

$$C_H = -4.7989 \times 10^{-4} + 6.3787 \times 10^{-6}\theta - 1.1647 \times 10^{-7}\theta^2 + 5.717 \times 10^{-10}\theta^3 \tag{12c}$$

$$s = A_S \xi + B_S \xi^{3/2} + C_S \xi^2 \tag{13}$$

$$A_S = 1.42185 \times 10^{-3} - 3.1137 \times 10^{-7}\theta + 4.2446 \times 10^{-9}\theta^2 \tag{13a}$$

$$B_S = -2.1762 \times 10^{-4} + 4.1426 \times 10^{-7}\theta - 1.6285 \times 10^{-9}\theta^2 \tag{13b}$$

$$C_S = 1.0201 \times 10^{-5} + 1.5903 \times 10^{-8}\theta - 2.3525 \times 10^{-10}\theta^2 \tag{13c}$$

where ξ is the salinity (part per thousand) of a specific stream (expressed as g of solute salt per kg of solution, which is equal to 1000x; we consider this as a good approximation, but according to Millero, total grams of salt per kg of seawater is salinity multiplied by 1.004880) and θ is temperature in Celsius (0–40 ℃).

Table 1. Parameters for the calculation of maximum power from salinity gradient for three case studies.

	Units	Symbol	General system (mixing)	PRO type system	RED type system
Mass flow–seawater (stream A)	kg/s	F_A	$F_A \gg F_B$	1,000	1,000
Salinity–stream A	g/kg	ξ_A	35	35	35
Mass flow–soft water (stream B)	kg/s	F_B	1,000	1,000	1,000
Salinity–stream B	g/kg	ξ_B	0	0	0
Salt transfer ratio from A to B		τ_s	0	0	variable
Water transfer ratio from B to A		τ_w	$\rightarrow 1$	variable	0
Temperature	℃	θ	10	10	10
Pressure	atm	p	1	1	1
Calculated maximum power	kW	W	2,341	figure	figure

4.2. First example: system allowing transfer of pure water into a sink of oceanic water

In the first situation, we calculate the maximum power that can be recovered from a system (or device) involving the transfer of 1,000 kg/s of pure water (salinity zero) to a sink of oceanic water with a salinity of 35 g/kg. We suppose $F_A \gg F_B$ in the mass balance calculations. Fixing τ_w at a value close to 1 means that $F_{B'}$ will become close to zero according to Equation (4). As shown in Table 1, calculated maximum power is 2,341 KW or 2,341 kJ (0.65 kWh) per 1,000 kg of fed soft water (inlet stream B). This is equivalent to a gravitational potential energy corresponding to a height of 239 m according to Equation 10, or a kinetic energy corresponding to a velocity of 68 m/s according to Equation 9.

Figure 2. Variation of theoretical reversible power with water transfer ratio (PRO type system) or salt transfer ratio (RED type system).
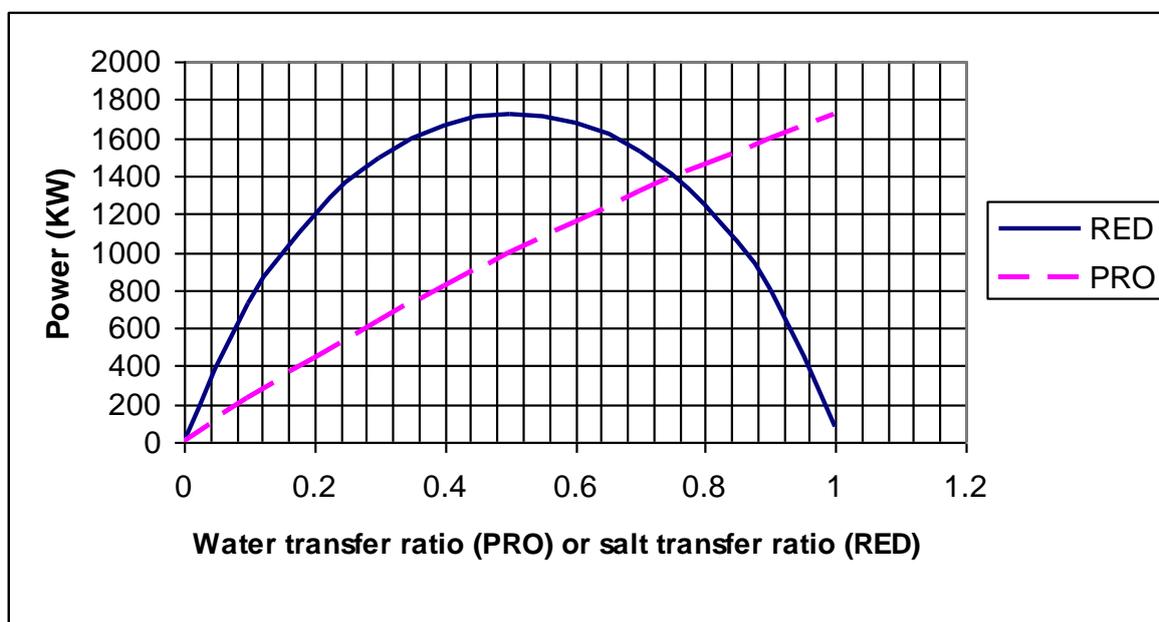
4.3. Second example: a PRO type system

We consider the situation of a membrane based system for which flow of each of the inlet streams A and B is 1,000 kg/s as presented in Table 1. We consider the ideal situation of no transport of salt ($\tau_s = 0$) Figure 2 shows the effect of τ_w on the power. Table 2 shows calculated values of h, s and $e_t + e_{ch}$ for stream A' for different values of τ_w, as intermediary results. Value of exergy is zero for streams B and B' (pure water). Enthalpy and entropy for stream A are equal to the corresponding variables for stream A' when τ_w is zero. We can see from Figure 2 that, in this case, a higher recovery of water will allow a higher mechanical power. For a practical water recovery rate of 0.8 we have 1,458 KW or 1,458 kJ (0.405 kWh) per 1,000 kg of inlet stream B.

Table 2. Calculated values of specific enthalpy, entropy and exergy of stream A', for different values of τ_w (PRO type ideal system).

τ_w	h (100 kJ/kg)	s (100 kJ/kg–K)	$e_t + e_{ch}$ (kJ/kg)
0	–4.6184	1.8096	–5.1673
0.1	–1.4631	1.7276	–4.9037
0.2	0.6918	1.6533	–4.6720
0.3	2.1841	1.5856	–4.4653
0.4	3.2258	1.5234	–4.2791
0.5	3.9543	1.4662	–4.1098
0.6	4.4612	1.4133	–3.9549
0.7	4.8088	1.3642	–3.8125
0.8	5.0408	1.3185	–3.6809
0.9	5.1877	1.2759	–3.5589
→1	5.2719	1.2361	–3.4454

4.4. Second example: RED type system

In this last example, we consider the situation of a membrane based system for which flow of each of the inlet streams is 1,000 kg/s as presented in Table 1. We consider ideal case where there is no transport of water ($\tau_w = 0$) Figure 2 shows the effect of τ_s on the power. Table 3 shows calculated values of h, s and $e_t + e_{ch}$ for each of the outlet streams A' and B', for different values of τ_s, as intermediary results. Value of exergy is zero for streams B (pure water). Enthalpy and entropy for stream A are equal to the corresponding variables for stream A' when τ_s is zero.

We can see that in this case, there is an optimum of 1,723 kW for a salt recovery rate of 0.5. Such an optimum is to be expected since an increase in the transport rate of salt transport will involve simultaneously an increase in the salinity of stream B' and a decrease in the salinity of stream A, meaning a decrease in the global salinity gradient in the system. For a practical salt recovery rate of 0.3 we have 1,488 KW or 1,488 kJ (0.413 kWh) per 1,000 kg of inlet stream B.

Table 3. Calculated values of specific enthalpy, entropy and exergy of streams A' and B' for different values of τ_s (RED type ideal system).

Streams →	A'			B'		
τ_s	h (100 kJ/kg	s (100 kJ/kg–K)	$e_t + e_{ch}$ (kJ/kg)	h (100 kJ/kg	s (100 kJ/kg–K)	$e_t + e_{ch}$ (kJ/kg)
0	–4.6184	1.8096	–5.1673	0.0000	0.0000	0.0000
0.1	–1.2789	1.7220	–4.8860	1.6731	0.3684	–1.0258
0.2	1.3734	1.6246	–4.5840	3.2759	0.6449	–1.7923
0.3	3.3406	1.5154	–4.2551	4.4765	0.8707	–2.4192
0.4	4.6285	1.3915	–3.8918	5.1664	1.0604	–2.9493
0.5	5.2485	1.2497	–3.4842	5.2896	1.2227	–3.4075
0.6	5.2204	1.0855	–3.0198	4.8136	1.3634	–3.8102
0.7	4.5776	0.8929	–2.4810	3.7186	1.4865	–4.1696
0.8	3.3783	0.6628	–1.8418	1.9931	1.5954	–4.4949
0.9	1.7360	0.3796	–1.0569	–0.3693	1.6925	–4.7934
1	0.0000	0.0000	0.0000	–3.3714	1.7799	–5.0709

5. Conclusions

From the examples presented above, we can see how easy it becomes to calculate the maximum power obtainable from a salinity gradient, using a simple exergy balance. Furthermore, since we use pure thermodynamics, it becomes possible to compare technologies or different approaches being proposed for the production of power from a salinity gradient. Nevertheless, we should keep in mind that practical performance of systems could be far from the maximum values calculated thermodynamically. Apart from any consideration related to irreversibility encountered in any system, we should mention here that, in a membrane process, the effect of concentration polarization related to mass transfer phenomena involved is known to have a detrimental effect on the performance of such systems. Evaluating maximum achievable performance using thermodynamics is useful because we already know what we can expect from a given system. This exercise can then be part of preliminary investigation for the choice of a technology for a specific application.

Acknowledgements

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