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Leveraging MultiSource Heat Pump Technology to Produce Electricity and/or Hydrogen Through Enhanced Reverse Electrodialysis Process -

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Abstract

Reverse electrodialysis (RED) technology provides a way to harness clean and sustainable energy from salinity gradients. First introduced in 1954 [4], this technology has not been widely applied due to limitations requiring direct access to fresh and seawater. The novel approach of introducing a MultiSource heat pump technology into a RED-based system allows users to take full control of the salinity gradient by dissolving and regenerating the salt in a closed-loop system. The heat pump exploits otherwise wasted low-grade heat energy to simultaneously heat and cool salt solutions to produce electricity and/or hydrogen by reverse electrodialysis process. The untapped potential of excess heat as a source of energy is substantial, with Europe and The United States alone boasting an estimated 5791 TWh of accessible waste heat per year [13, 21, 22]. This innovative approach unleashes the full potential of salinity gradient energy, thus offering a solution to the current bottleneck of the seaside water source dependency. Approximately one-third of the global electricity is consumed by residential buildings [8,9]. The unique combination of the reverse electrodialysis process and MultiSource heat pump technology paves the way to significantly reduce energy consumption as well as greenhouse gases (GHG) emissions on a global scale. In this work, we will explore some of the theoretical aspects in more detail.

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Keywords: RED; Heat pump; Reverse Electrodialysis; Salinity Gradient Energy; Blue Energy; Clean Energy; Renewable Energy; Circular Economy; Global Warming; MultiSource HeatPump;

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1. Introduction

Air conditioning is a process which allows cooling, heating, and ventilation of an environment. Although the term “air conditioning” is predominantly associated with the cooling process, the process of air conditioning systems also involves humidity control and air cleaning as its key functions. Currently, the use of air conditioners and electric fans for cooling purposes represents 20% to 40% of the global building electricity consumption, which is only projected to increase with elevated global temperatures [2,9]. Presently, air conditioning is used in approximately 90% of homes in the United States, whereas in locations such as India, air conditioning is less prevalent, with an average of around 5% of homes utilizing this technology [3]. Worldwide demand for cooling is rising fast [3]. Currently, more than one-third of the electricity generated in the world is consumed in the residential sector and most of this energy is used for water heating, air conditioning, and space heating [8,9]. Earth’s population and global warming are only expected to increase while global energy demand from air conditioners is anticipated to triple by 2050 [3]. In these situations, the demand for air conditioning will surge while imparting a significant impact on the world’s overall energy reliance, putting pressure on the electrical grid, and driving up global greenhouse gas (GHG) emissions. On the other hand, at the 2022 United Nations Climate Change Conference of the Parties (COP27), the United States launched the Net-Zero Government Initiative, inviting governments to lead by example and achieve net-zero emissions from national government operations by no later than 2050 [14]. Therefore, renewable energy resources have been one of the most important, widely researched, and discussed global topics for over a decade. With the ever-increasing problem of global warming, there has been a global effort in steering away from carbon-based fuels. There are a wide variety of natural sources for clean energy including solar and wind energy. While it is crucial that we continue to make a switch to these resources, it is important to note that their availability, such as usage during specific times of the day, and reliability are limited. They also require massive amounts of energy storage for them to be a sustainable solution to our energy crisis. Therefore, if we want to address the issue of global warming and achieve a net-zero objective, we must address both restrictions: the availability of energy and GHG-neutral air conditioners. The untapped potential of excess heat as a source of energy is considerable, with Europe alone boasting an estimated 2860 TWh of accessible waste heat per year [13]. This energy source is widely available and abundant, with the added advantage of being constantly accessible, often in the form of unwanted waste. The convergence of a MultiSource heat pump and enhanced Reverse Electrodialysis (RED) promises to become a solution to this problem. The RED Heat Hump (RED-HP) technology relies on waste heat and low-grade heat energy to produce electricity and/or hydrogen, with the added benefit of being entirely carbon-neutral. This technology promises to cool a structure and convert waste and low-grade heat into usable energy. The game-changing RED-HP technology has the ability to significantly reduce energy usage and GHG emissions on a global scale.

2. Salinity Gradient Power

Salinity Gradient Power (SGP) is defined by Gibbs free energy of mixing between two water sources of differing salt concentrations. The concept of SGP was first proposed by R. E. Pattle in 1954 and has since expanded into a variety of methods by which to harness this chemical potential of mixing two water streams with different salinity [4].

During the uncontrolled mixing, $\Delta \boldsymbol{G_{mix}}$ (Gibbs energy of mixing) is released into the environment. This released chemical energy represents the maximum potential energy that can be harvested. The Gibbs free energy [J] released per mole during the mixture of two solutions is given below:

$$\Delta G_{mix} = G_b - (G_c - G_d) \tag{1}$$

Where ΔG_{mix} is the free eneregy of mixing [J/mol], G_b is the Gibbs energy of the mixture, the brakish water [J/mol], G_c is the Gibbs energy of the concentrated salt solution (e.g. brine) [J/mol] and G_d is the Gibbs energy of the diluted salt solution (e.g. fresh water or river water).

$$\Delta G_{mix} = \Delta H - T \cdot \Delta S = -T \cdot (S_b - S_d - S_c) \tag{2}$$

$$S \quad = -R \cdot N_T \sum_i x_i ln\,(x_i \cdot \gamma_i\,) \tag{3}$$

Where S is the entropy (J/K), T is the temperature of mixture (K), R is the universal gas constant (8.314 J/(mol·K)), N_T is total number of moles (mol), x_i is the mole fraction of component i, γ_i is the activity coefficient of component i, which accounts for the non-ideal behavior of the solution. The change in enthalpy ΔH (J) is not taken into account in equation 2. The objective of equation 2 is to calculate the theoretically available energy from mixing two dissolved salt solutions with different salinities.

The three primary means of harnessing salinity gradient power from this extraordinary heat pump assisted close loop process are the reversal of the capacitive deionization (RCD) [10], pressure-retarded osmosis (PRO), and reverse electrodialysis (RED). For the basis of this paper, only RED will be discussed in detail as it is believed to have the greatest potential based on its high efficiency [17, 18].

3. Reverse Electrodialysis (RED)

Reverse electrodialysis was first proposed and demonstrated by Richard Pattle between 1954 and 1955, but it was not until a push from the first and second oil crises in 1973 and 1979 that interest in RED was truly heightened [4]. Today several institutions have committed to the RED technology as a way to harness the salinity gradient power (SGP). SGP is a sustainable energy source with a large worldwide potential of 22776 TWh per year, and it is available at deltas where river flows into the sea [20]. Commonly referred to as “Blue Energy”, this renewable and carbon-free energy source provides a significant advantage over other renewable sources such as wind and solar power, as it is constantly accessible. The current limitation of this technology is that it can only be applied in specific locations where water with different levels of salinity is available, namely areas where there is access to both low and high salt concentration water.

Reverse electrodialysis utilizes the salinity gradient of two water solutions to produce power in the form of electricity (Figure 1). When salt dissociates in water two ions are formed (anions and cations) containing positive and negative charge. Naturally, concentrations of ions dissociated in the water tend to flow from high concentration to low concentration and can also be further explained by the Donnan exclusion principle [7]. Anions migrate through the anion exchange membrane (AEM) toward anode(s) and cations move through the cation exchange membrane (CEM) towards cathode(s). For example, a positively charged cation can only move through a cation exchange membrane however a negatively charged anion would be blocked by repulsion. It is the opposite for an anion exchange membrane as positive cations are blocked and negatively charged anions can pass thorough. This dynamic allows for the controlled mixing of salts in the RED cell which creates an ionic potential. As ions flow from the concentrated to dilute solution, ions from a separate recirculating rinse solution are pulled from one electrode to the other. This overall movement of ions creates a stack potential that can be harvested through an external load connected to both electrodes and can be calculated using the Nerst equation:

$$\Delta V^0 = N\frac{\alpha RT}{zF}\ln\,\left(\frac{a_c}{a_d}\right) \tag{4}$$

Where ΔV^0= is the theoretical stack potential [V], N is the number of membranes [-], α is the membrane selectivity [-], R is universal gas constant [8.314J/(mol·K)], T is the absolute temperature [K], z is the electrochemical valence [-], F is the Faraday constant [98485 C/mol], a_c is the activity of the concentrated solution [mol/L]

A RED cell can operate in various modes, the flow of the two solutions can be directed in co-flow, counter-flow, or cross-flow. Furthermore, electrodes can be composed of a single part or multiple segments, with studies showing that multiple segmented electrodes can enhance the efficiency of the cell stack and increase the overall power density [6].

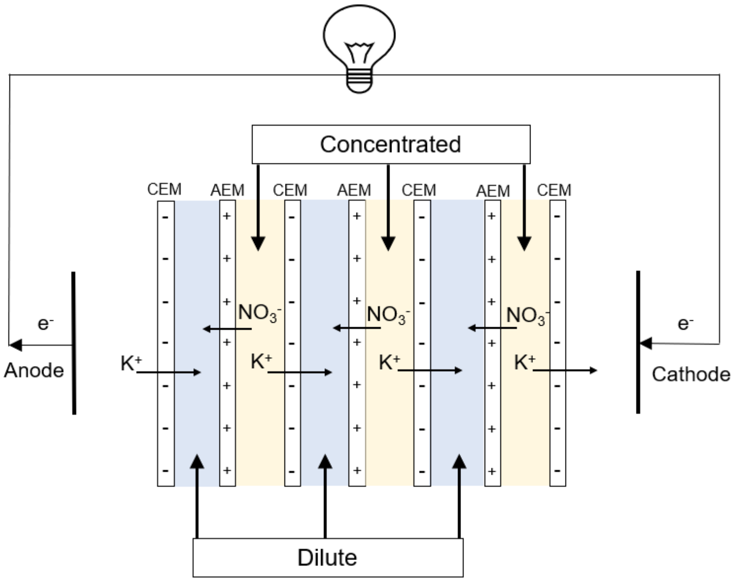

Figure 1. Process of reverse electrodialysis.

At auxiliary electrodes (anode and cathode) red-ox couple solution such as hexacyanoferrate(II) and hexacyanoferrate(III) can be used to minimize losses and produce electricity. In addition, it should be noted that hydrogen gas can also be generated through the process of water splitting reactions:

$$\text{Anode:} \quad 2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^- \tag{5}$$

$$\text{Cathode:} \quad 4H_2O + 4e^- \rightarrow 2H_2\uparrow + 4OH^- \tag{6}$$

Numerous publications have covered the topic of hydrogen production using reverse electrodialysis [16, 19], and thus our study will not specifically address this area.

The power output of a RED cell stack depends on the stack resistance and electromotive force. The stack resistance R_{stack} [Ω]is a function of the cell resistance R_{cell} [Ω], the number of cell pairs N, A_{mem} is the effective membrane area [m^2] and the resistance of the electrode system $R_{electrode}$.

$$R_{stack} = \frac{N}{A_{mem}} \cdot R_{cell} + R_{electrode} \tag{7}$$

The cell resistance R_{cell} [$\Omega \cdot m^2$] is a function of the resistance of the cation R_{CEM} and anion membrane R_{AEM} [$\Omega \cdot m^2$] and the resistance of the concentrate and dilute cell compartments (R_{con} and R_{dil})

$$R_{cell} = R_{AEM} + R_{CEM} + R_{con} + R_{dil} \tag{8}$$

The resistance of concentrate R_{con} [$\Omega \cdot m^2$] and dilute solution R_{dil} [$\Omega \cdot m^2$] can be calculated as below:

$$R_{con} = \frac{d_c}{\kappa_c} \tag{9}$$

$$R_{dil} = \frac{d_d}{\kappa_d} \tag{10}$$

As shown, R_{con} and R_{dil} are a function of the compartment thickness d_c [m] and solutions conductivity κ [$S \cdot m^{-1}$].

The maximum power output [W] and power density (W/m^2) can be calculated using the following equation:

$$P_{max} = \frac{(V^0)^2}{4R_{stack}} \quad (11)$$

$$PD_{max} = \frac{P_{max}}{A_{total}} \quad (12)$$

Where A_{total} is the total membrane used and the external load and internal load is assumed to be equal.

4. Heat Pump

Heat pumps offer an energy-efficient alternative to furnaces and air conditioners for all climates. They provide optional year-round cooling or heating utilizing a vapor compression cycle, thermoelectric cooler, and/or chemical absorption process. Heat pumps do not create heat, they redistribute and move heat. Passively, heat moves from hot to cold. With a heat pump, one can actively cool and heat a structure by moving heat from cold to hot. The Coefficient of Performance (COP) of a heat pump can be used to determine a heat pump's efficiency [1]:

$$COP = \frac{Output\ Capacity\ (W)}{Power\ Input\ (W)} \quad (13)$$

Figure 2 provides a visual representation of the heat pump's operation process. As shown, with an input power of 1500 watts, 3000 watts of heat equivalent is harnessed from a cold stream. The heat pump is capable to concentrate the heat and multiply it by a factor of 3 to produce 4500 watts of heating. In the present scenario, the $COP_{Heating}$ is 3, although it should be noted that depending on the season, the $COP_{Heating}$ can reach values as high as 7 [23, 24, 25].

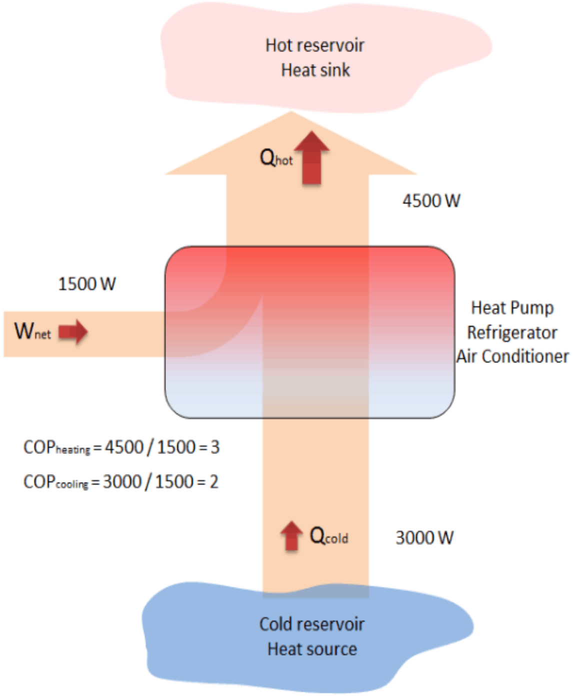

Figure 2. Heat pump COP diagram.

5. Reverse Electrodialysis Heap Pump (RED-HP)

RED is a promising technology for generating renewable energy from the salinity gradient in natural water sources, such as rivers and oceans, without the need for combustion or fuel consumption. The technology has the incredible global potential of 22776 TWh per year of electricity to contribute to a more sustainable and low-carbon energy system, particularly in coastal regions where there is a significant salinity difference between seawater and freshwater [20].

Several attempts have been made to upscale the RED technology to a commercial level [5]. However, no one has yet managed to bring it to a commercially viable level, partly due to the high price of the ion exchange membrane, which is a significant barrier to commercialization. As a general estimate, the cost of an ion exchange membrane can range from around \$20 to \$200 per m^2. To date, the majority of the research and pilot systems have been performed as an open loop system utilizing seawater and fresh water. The dependence on both fresh and seawater not only poses limitations on the applicability of this technology but also restricts the potential locations for implementation. Furthermore, the power output of the system is constrained by the specific types of salts and their concentrations that can be utilized by the technology. Additionally, the use of seawater and freshwater requires large utility costs to pretreat the water. Several steps of microfiltration, ultrafiltration and reverse osmosis filtration is required to remove unwanted sediments, organics and objects out of the natural water streams. This results in the need for large quantities of membranes in order to generate power. Therefore, using closed loop system with a selected salt type and its concentration to deliver the highest available salinity gradient will unlock the potential of reverse electrodialysis globally.

MultiSource heat pump technology utilizes thermal energy and waste heat using proprietary thermal chemical optimization techniques that greatly reduce or eliminate the resulting carbon footprint while providing simultaneous heating and cooling [25]. By introducing MultiSource heat pump technology to a RED-based system, high levels of power efficiency can be achieved in a closed-loop system [25]. Simultaneous heating and cooling provided by the heat pump can be used to create an optimal artificial salinity gradient. Figure 3 shows a schematic representation of the RED-HP closed loop system.

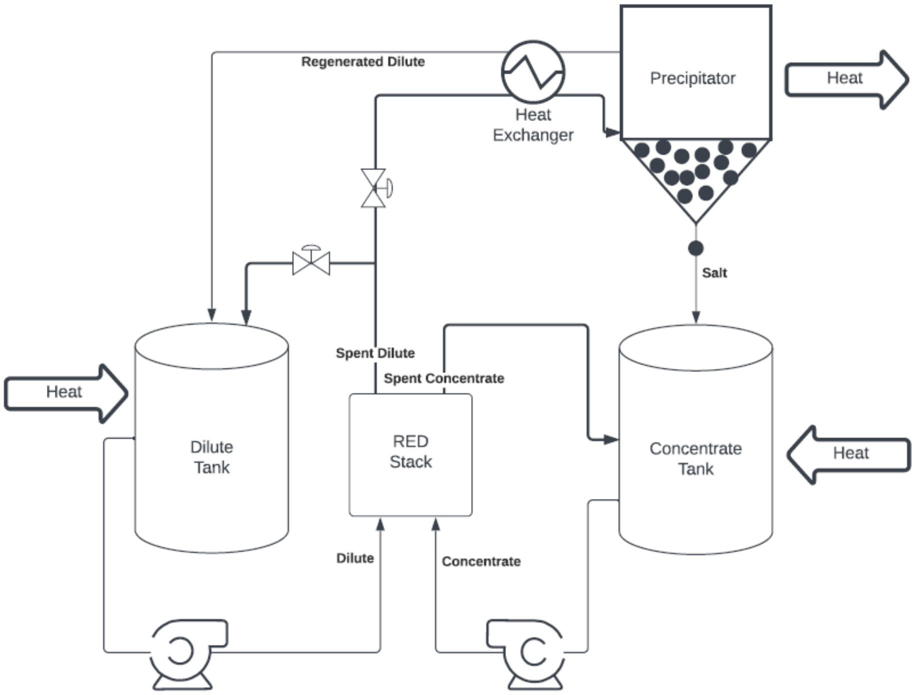

Figure 3. The closed-loop RED-HP system concept.

In this process, a salinity gradient can be regenerated by leveraging the power of a heat pump and using a salt with a steep solubility curve. As shown in the Figure 4 salts such as potassium nitrate and calcium chloride have a steep exponential solubility curve. Consequently, a highly concentrated salt solution can be achieved at temperatures greater than 65ºC and a dilute solution can be achieved by precipitation of salt at lower temperatures ranging from 5-20ºC. To reduce energy consumption, the heat from the spent dilute solution can be exchanged with the refreshed dilute solution, as illustrated in Figure 3. The main contributor to the energy input is heating up dilute solution from, for example, 10ºC to approximately 65ºC. The energy required to heat up 1m^3 of water from 10ºC to 65ºC is 63.9 kWh in the absence of a heat pump. However, the use of an efficient heat pump with a COP$_{\text{Heating}}$ of 7 reduces the required electrical energy to heat up 1m^3 of water from 10°C to 65°C to only 9.1 kWh. Furthermore, during the process, the spent dilute solution can be used as a heat source, resulting in a more energy-efficient system. It is important to note that excess heat is one of the largest untapped energy sources and it can be leveraged by utilization of MultiSource heat pump technology [25]. Moreover, it is highly advantageous to have a closed-loop system as the water pre-treatment cost are removed, and various selected salts can be used in a controlled manner.

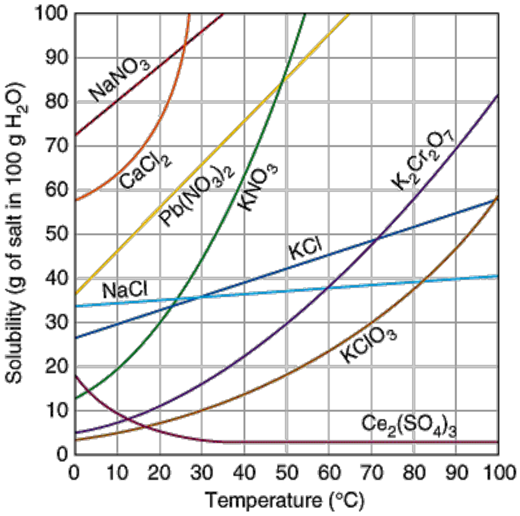

Figure 4. Various salt solubilities at varying temperatures.

The results from the modeled data are presented in Table 1. Salinity gradient, which refers to the difference in salt concentration, is a critical parameter for achieving high power density. To reach a highly concentrated solution of potassium nitrate, the RED process should be operated at an elevated temperature of 65ºC where 12 mol/L KNO_3 solution can be obtained. On the other hand, dilute solution concentration of 2 mol/L is limited by solubility of KNO_3 at low temperature of 10ºC. Both solutions have relatively high molarities above 0.5 mol/L, and therefore, activity coefficients were calculated using the Stokes-Robinson [16]. A higher temperature has a positive impact not only on the potential of the RED stack, which is calculated from the Nernst equation (Equation 4), but also on the membrane resistance, which decreases with increasing temperature [15]. The biggest contributors to RED stack resistance are membranes and dilute compartment resistance, which is related to compartment thickness [11]. Therefore, since we operate at higher salt concentrations and elevated temperatures, we assumed anion and cation exchange membrane resistance of 1 Ω·cm^2. Membranes with resistance of 1 Ω·cm^2 or lower are already commercially available [11]. The thickness of the dilute compartment was set in the RED model to 150μm to limit the dilute compartment resistance. The resistance of the electrodes is assumed to be negligible as a full-size stack will contain at least multiple hundreds of membranes reducing the contribution of the electrode resistance to less than 2%. The average membrane permselectivity is assumed to be 90%. Our RED model, based on equations 4-8, gives a maximal theoretical power density for 400 cell pairs, equivalent to 200m^2 of membrane area. The maximal achievable power density is 5.3W/m^2 of membrane area and the power output of a single stack is 1.06kW. It is important to note that the RED stack dimensions are 0.5m width, 0.5m height and 0.25m length (including 0.05m for auxiliary electrodes). These dimensions translate to a power density of 16.9kW per m^3 of RED stack. However, in practical application of RED, factors such as spacer shadow effect, current leakage, and concentration polarization phenomenon might limit this power density [15]. Energy spent on pumping dilute and concentrated solution was not taken into account; however, it is estimated to be less than 3-10% of the total power output of the RED system [18].

Dilute and concentrated buffer tanks need to have enough buffer capacity to operate at the most optimal salinity gradient. The theoretical available amount of energy available from the mixing of two salt solutions can be calculated from the Gibbs energy of mixing and thus the theoretical potential of salinity gradient energy can be evaluated. The energy theoretically obtainable from the mixing of 1 m^3 of 12 mol/L concentrated solution with 1 m^3 of 2 mol/L dilute solution at a temperature of 65ºC, calculated from Equation 1-3, equals 9.1kWh (32.8MJ). This allows a 1.06kW system to operate for multiple hours without the need for dilute compartment regeneration and loss of the salinity gradient. However, there is energy needed to heat up the solution after dissolving KNO_3. The enthalpy to dissolve KNO_3 in water equals to -34.9 kJ/mol (-9.69Wh/mol) [16]. This means that potassium nitrate is an endothermic salt and when it dissolves in water, it absorbs heat from its surroundings. If 1m^3 of 12 mol/L concentrated solution is mixed with 1m^3 of 2 mol/L dilute solution, then both solutions end up with a concentration of 7 mol/L. Therefore, to regenerate 1m^3 of dilute solution, 505.5 kg of KNO_3 salt (5000mol) need to be precipitated and dissolved in the concentrated solution tank. The energy required to heat up 1m^3 of concentrated solution is 48.4kW. This means that in order to harvest 9.1kWh of electricity, 48.4kWh of heat needs to be used to heat up 1m^3 of concentrated solution. It is important to note that by using efficient MultiSource heat pump technology with a $COP_{Heating}$ of 7, only 6.89kWh of electrical energy will be spent to compensate for dissolving of 505.5 kg of KNO_3 salt. This energy can be transferred from the dilute solution where the precipitation (dilute solution regeneration) process takes place at a low temperature of 10ºC. On the other hand, it is advantageous if an exothermic salt is selected because the concentrated solution will be heated up by the energy during dissolution.

In addition, it should be noted that energy recovery from salinity gradient energy in reverse electrodialysis is between 20% and 80% [17]. A reverse electrodialysis system was studied for a period of 30 days using natural seawater and river water, and the energy recovery values ranged between 30% and 37% [18]. The obtainable energy recovery from salinity gradient energy depends mainly on the operational current density and the internal stack resistance, which is dominated by the dilute solution resistance and the resistance of membranes.

Table 1: Model input values and the outcome results.

Name	**Symbol**	**Value**	**Unit**
Input parameters			
Concentration of concentrated solution	C_c	12	mol/L
Concentration of diluted solution	C_d	2	mol/L
Activity coefficient of concentrated solution	γ_c	0,4	-
Activity coefficient of diluted solution	γ_d	0,4	-
Specific conductivity of concentrated solution	κ_c	54,1	S/m
Specific conductivity of diluted solution	κ_d	23,2	S/m
Temperature	T	338,15	K
Average membrane permselectivity	α	0,9	
Resistance of anion exchange membrane	R_{AEM}	0,0001	$\Omega{\cdot}m^2$
Resistance of cation exchange membrane	R_{CEM}	0,0001	$\Omega{\cdot}m^2$
Thickness of spacer - concentrated solution	d_c	0,00015	m
Thickness of spacer - diluted solution	d_d	0,00015	m
Number of cell pairs	N	400	-
Single membrane active area	A_{mem}	0,25	m^2
Total membrane area	A_{total}	200	m^2
Results			
Open circuit potential	ΔV^0	37,6	V
Resistnace of the RED stack	R_{stack}	0,335	$\Omega{\cdot}m^2$
Maximum power output	P_{max}	1055	W
Power density	PD_{max}	5,3	W/m^2
Power per volume of stack	PV_{max}	16882	W/m^3

6. Conclusions

The potential of excess heat energy worldwide is substantial and could play a significant role in reducing global energy consumption and greenhouse gas emissions if efficiently harnessed. This energy source is widely available and abundant, with the added advantage of being constantly accessible, often in the form of unwanted waste.

This work identifies and quantifies the potential and operating window of RED as a sustainable energy source for excess heat recovery, utilizing heat pump technology to maintain a constant salinity gradient. The closed-loop 1kW RED-HP system concept was presented, and theoretical power output model was made. The theoretical open circuit potential was 36.7V and the theoretical power density was 5.3 W/m^2 of membrane area and 16.9 kW/m3 of RED stack. To achieve these power density numbers 400 cells pairs of membranes with 0.25m^2 area per cell are required as well as volume of 1m^3 of concentrated (12mol/L KNO_3) and 1m^3 of dilute solution (2mol/L KNO_3). Potassium nitrate salt was selected due to its solubility and temperature relationship, which allows for dilute and concentrated solution regeneration at a lower temperature. However, potassium nitrate is an endothermic salt and when it dissolves in water, it absorbs heat from its surroundings, which works against our heat transfer. The ideal salt for this process should be an exothermic salt that releases energy during dissolving and heating up of a concentrated solution, while absorbing energy during crystallization and cooling down the dilute solution at the same time.

The results of this study have significant implications for reducing global energy consumption and greenhouse gas (GHG) emissions. The RED-HP concept is currently in the process of prototype validation to further investigate its practical applications.

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