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Assessment of Current Blue Energy Technologies and Their Potential Applications on Romanian Water Resources

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Abstract: This study offers a comprehensive analysis of unconventional renewable and sustainable energy production options by tapping into the energy associated with the natural tendency to cancel salinity gradients that occur when salt water and fresh water come into contact. Furthermore, this paper assesses the potential for generating blue energy in Romania by examining historical data on flow rates from relevant fresh water sources, such as the Danube River, and the salt loading of potential receiving water bodies, including salt lakes, and the Black Sea. In addition, this study briefly references pilot-level technologies for blue energy production in other countries, including Norway, Japan, and the European Union. Based on literature data, this paper highlights the most important technological methods with applicative potential for harnessing energy from salinity gradients. The performances and limitations of these methods have been presented, acknowledging that despite recent years of advancements in materials and technologies, large-scale implementation and commercialization efforts are still limited. The analyzed data reveals that Romania possesses substantial potential blue energy resources for both large capacity installations, such as the Danube River-Black Sea with a potential achievable capacity of about 50 MW, as well as smaller capacity devices situated around saline lakes and salt deposits. This study concludes that Romania has a unique opportunity to capitalize on its vast blue energy potential and drive sustainable energy development.

Keywords: renewable energy; blue energy; SGE; PRO; RED; CAPMIX



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1. Introduction

Research on renewable energy technologies has focused in recent years on resources for producing low-carbon renewable energy with the goal of meeting the European commitment to achieve climate neutrality by 2050 [1–4]. To combat climate change, an energy transition is necessary to replace fossil fuels with available renewable sources [5], including marine resources [6]. For several reasons, such as legislation, financial aspects, or environmental integration, marine energy exploitation is still insufficiently implemented; being largely unknown to the general public.

Romania has rich and varied renewable resources including biomass, hydro energy, geothermal, wind, solar, and photovoltaic. These resources are distributed throughout the country and can be exploited on a larger scale when the performance–price ratio is improved. Romania has advanced in its use of wind and photovoltaic technologies, which have a very low impact on the environment [7].

The need for clean energy grows, and low-emission renewable energy is a sustainable alternative to meet our daily energy needs. The capacity of renewable energy technologies to offer varied alternative solutions is gradually improving (Table 1).

Table 1. Types of techniques for converting renewable sources into energy [8,9].

Energy Type	Source	Technology	Energy Product	Application
Bioenergy	waste and biomass	Combustion	Heat (cooking, space heating) Process heat, steam, electricity	Widely applied
		Gasification/power production	Electricity, heat (CHP).	Demonstration phase
		Gasification/fuel production	Hydrocarbons, methanol, H ₂	Development phase
		Hydrolysis and fermentation	Ethanol	Commercially applied; under development
		Pyrolysis/production of liquid fuels	Bio-oils	Pilot phase; some technical barriers
		Pyrolysis/production of solid fuels	Charcoal	Widely applied
		Extraction	Biodiesel	Applied, expensive
		Digestion	Biogas	Commercially applied
Solar	sun	Photovoltaic solar energy conversion	Electricity	Widely applied; rather expensive;
		Solar thermal electricity	Heat, steam, electricity	Demonstrated;
		Low-temperature solar energy use	Heat (water and space heating, cooking, drying) and cold	Commercially applied and demonstrated
		Passive solar energy use	Heat, cold, light, ventilation	Demonstrations and applications;
		Artificial photosynthesis	H ₂ or hydrogen rich fuels	Fundamental and applied research
Wind	wind	Water pumping and battery charging	Movement, power	Small wind machines, widely applied
		Onshore wind turbines	Electricity	Widely applied commercially
		Offshore wind turbines	Electricity	Development and demonstration phase
Hydropower	water	Hydro plants and dams	Power, electricity	Commercially applied
Geothermal	earth	Geothermal and head pumps	Heat, steam, electricity	Commercially applied
Marine	waves, tides, salinity, currents	Tidal energy	Electricity	Applied, expensive
		Wave energy	Electricity	Research, development, and demonstration phase
		Current energy	Electricity	Research and development phase
		Ocean thermal energy conversion	Heat, electricity	Research, development, and demonstration phase
		Salinity gradient/osmotic energy	Electricity	Theoretical option
		Marine biomass production	Fuels	Research and development phase

In recent years, significant progress has been made in the development of power generation technologies to enhance the energy extraction from renewable sources. This is important because, although many older conventional renewable technologies have larger public use, great amounts of energy are required for their modules manufacture as in the case of semiconductor solar panels. In this context, hybrid unconventional green technologies are developed that harness multiple types of power sources simultaneously,

such as the photovoltaic microbial fuel cells [10–12] that harness chemical, biological and solar energy sources. This field of research demonstrates the potential for advancements through the utilization of newly developed nano-structured materials and catalysts. These advancements not only enhance biocompatibility and energy transfer efficiency but also reduce the capital costs associated with many conventional green energy technologies.

One of the unconventional sources of renewable energy is called “Blue Energy” or “Power from Salinity Gradient” (SGP) [9]. In broad terms, it is energy obtained by controlled mixing of a stream of high salinity (HS) water (e.g., seawater) and a stream of low salinity (LS) water (e.g., treated wastewater or freshwater from a river). There are two main applications: (1) as an “autonomous power plant” located at the point where a river flows into the sea or (2) as a hybrid energy generation process that focuses on recovering energy from a production process, such as desalination or a wastewater treatment plant.

At a global level, there are several technologies available for obtaining renewable energy from salinity gradient by mixing fresh and saline water, which provide a new strategic approach to obtaining new sources of renewable energy [13].

However, energy production from salinity gradients is not yet used in Romania, despite its remarkable potential for applicability. In other countries, technologies based on salinity gradients have already been applied, and research has been conducted both at the laboratory-level and at the micro-pilot-level for certain types of technological approaches.

The most well-known and investigated technologies for generating energy from the salinity gradient are Pressure Retarded Osmosis (PRO), Reversed Electrodialysis (RED), and Capacitive Mixing (CAPMIX). The theoretical amount of energy available from mixing 1 m³ of seawater with 1 m³ of river water is about 1.8 MJ [14,15]. For other applications, which could use saturated brine instead of seawater, the theoretical energy available from mixing it with river water is 15 MJ [16,17]. Other scientists report that the theoretical mixing energy of 1 m³ of river water with seawater corresponds to 0.70–0.75 kWh [18]. Based on simple estimations, the theoretical global power of mixing seawater and river water can reach 1.9–2 TW of electricity (~15.102 TWh/year), which is approximately 10% of the current global energy consumption [2,3,19].

This study analyzed the existing methods for obtaining renewable energy from salinity gradients, their advantages and disadvantages, as well as Romania’s potential to generate blue energy.

2. Technologies for Obtaining Energy from Salinity Gradient

2.1. Pressure Retarded Osmosis

The most intensively studied technique for obtaining energy from the salinity gradient is pressure retarded osmosis (PRO), which first converts blue energy to mechanical work using a semipermeable membrane and then to electric energy using a hydro-turbine (Figure 1) [20,21].

PRO is an energy generation process that harnesses the salinity gradient between two bodies of water with different salinities [22,23]. PRO uses a semipermeable membrane placed between the two streams of different salinity, where water permeates from the less concentrated stream to the more concentrated one, to balance the concentration gradient between the two solutions [24,25].

In PRO technology, a salinity gradient is used as the driving force to produce osmotic power [26]. This is caused by a difference in osmotic pressure between the two sides of the membrane, resulting in lower salinity water from the feed solution being driven towards a pressurized draw solution with higher salinity [26].

PRO generates continuous electrical energy regardless of the time of day and weather conditions [21].

In the last decade, significant progress has been made in the rational design and fabrication of efficient PRO hollow fiber membranes. Both fully-formed phase inversion hollow fiber membranes and composite thin film coated hollow fiber membranes with

suitable membrane structures, balanced permeation properties, and good mechanical strength have been developed [27].

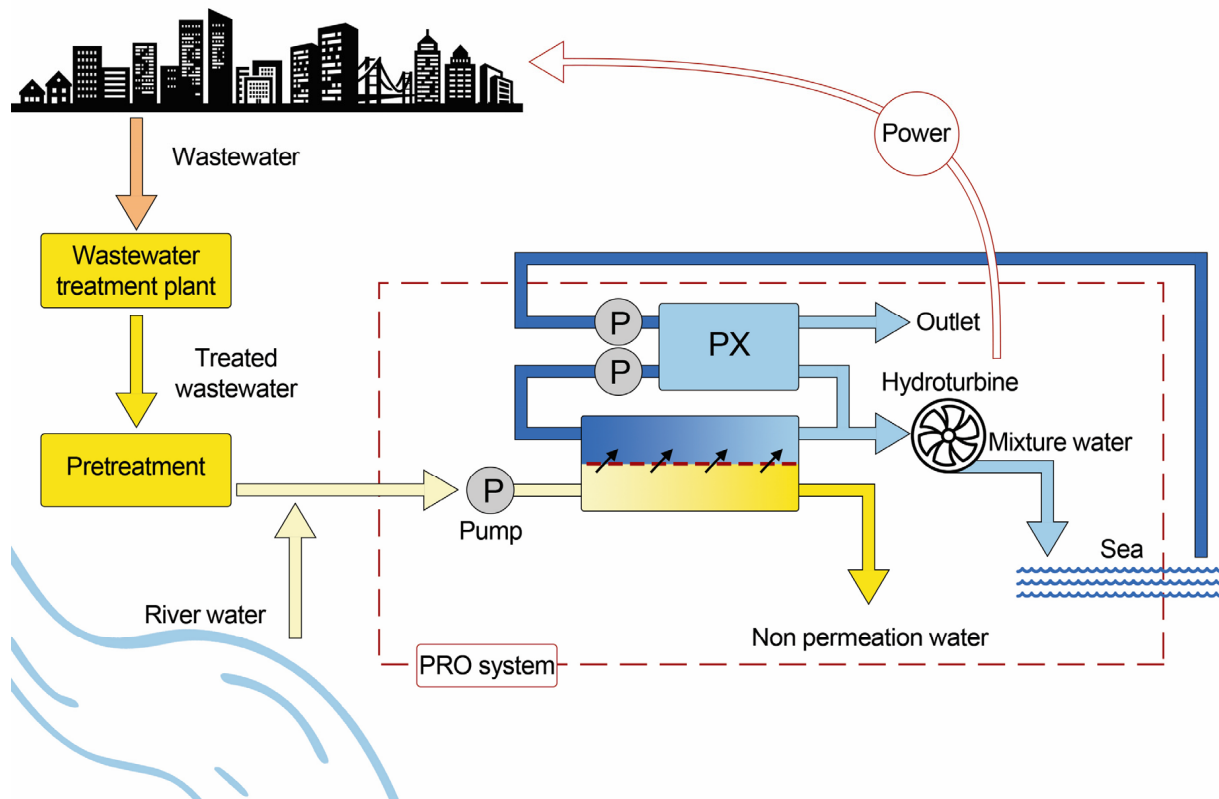


Figure 1. PRO system using seawater, river water and sewage-treated water, modified after [21].

However, a feasibility analysis of PRO-scale processes is hindered by the lack of a simulation-optimization framework for the PRO unit that takes into account the effects of: (1) non-ideality of the electrolyte solution on the evaluation of osmotic driving force, (2) non-development of the membrane idealness in evaluating permeate flux, (3) membrane pressure drop, (4) continuous dilution of the draw flow over large membrane surfaces, reducing the average driving force, and (5) inefficiency of pressured equipment. These phenomena have a significant impact on the amount of net recoverable energy from a particular PRO configuration [21].

Although there have been many recent advances in membrane performance and other system components for PRO, it is still uncertain whether the process can be implemented feasibly.

2.2. Reverse Electrodialysis (RED)

Direct electrodialysis uses an external current to force the ions migration through ion-selective membranes against their chemical potential. There are two types of membranes involved: anion exchange membranes (AEM) and cation exchange membranes (CEM). In an electrodialysis module, these membranes are alternately stacked with spacers delimiting water flow chambers. At the ends of the stack, electrode chambers are used to close the electrical circuit. In direct electrodialysis, an external electric current will draw the anions from chamber x through AEM toward the anode. After passing through an AEM membrane to chamber y , the next membrane will be a CEM which prevents the anions to pass further. At the same time, cations from the next chamber z will be drawn toward the cathode, passing through the CEM membrane in the y chamber. From there, the AEM membrane prevents the cations from reaching the x chamber. This is how direct electrodialysis forms chambers with alternating low (x, z) salinity (LS) and high (y) salinity (HS). In reverse

electrodialysis (RED), the HS water flow chambers are fed with sea water or brines and the LS water flow chambers are fed with river water (Figure 2).

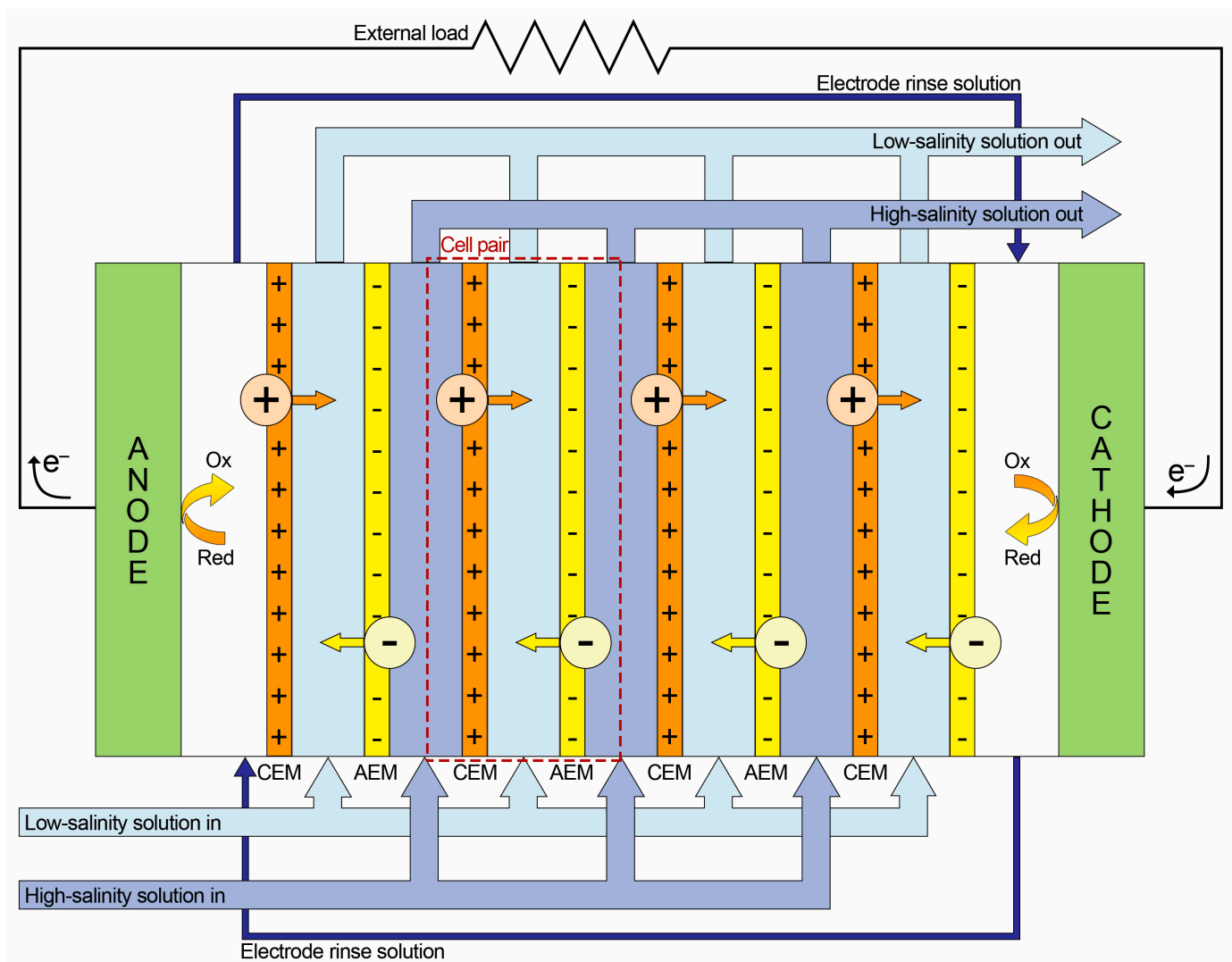


Figure 2. Schematic diagram of the RED system, modified after [28].

The arrows from the internal circuit depict the positive ions migration toward the cathode and the negative ions migration toward the anode. In the external circuit, the migration direction of the electrons as negative charged carriers is depicted. The electric current conventional direction in the external circuit is inverse to the electron migration direction.

Since CEM and AEM membranes allow either positively charged ions or negatively charged ions to pass from HS towards LS (driven by their chemical potential difference between HS and LS), ionic concentration differences over the membrane surfaces are created which polarize each membrane. The alternate stacking of the membranes cumulates the individual membrane's electrical potential differences towards a greater overall voltage. When the electrodes are connected to an electrical load which allows the flow of electrons in the external circuit, ions are transported in the internal circuit from HS toward LS chambers. At the ends of the stack, in the electrode chambers, the ionic current is converted to electrical current through reversible redox reactions to promote the energy generation [29,30].

The symmetry between ED and RED processes potentially allows the use of a specially designed electrodialysis module as an energy accumulator, functioning as an ED during the charge cycle and as a RED during discharge.

In modern times, pilot-level experimentation, such as the Netherlands Blue Energy project at Afsluitdijk and the European Union's REAPower in Marsala, Italy had encouraged the scientific community to develop RED technologies with higher membrane power density (over $2.2 \text{ W}\cdot\text{m}^{-2}$) and a decrease in fouling and other adverse influences by improving membrane design and introducing periodic steps aimed at membrane's surface reconditioning [30].

2.3. Capacitive Mixing (CapMix)

The advantages of CapMix over the PRO or RED technologies are derived from the fact that CapMix does not require the use of high pressures and turbines such as in PRO or special redox electrolytes such as in RED. CapMix is similar to PRO and RED due to the fact that it extracts energy from mixing waters with different salinity. Some of the differences between CapMix and RED are related to the fact that RED systems may operate continuously as opposed to CapMix which operates following cycles of charge and discharge. The CapMix cells use either the capacitive double-layer expansion (CDLE) or capacitive donnan potential (CDP) as the main mechanism for generating power from salinity differences [31]. In this respect, CDLE-CapMix technologies are similar to the behavior of electrical capacitors. In an electrical capacitor, the energy consumed during the charge cycle is slightly greater than the energy recovered during its discharge on an external resistor. In CapMix technologies, because the charging and discharging of the electrodes takes place in waters with different salinity, the discharging step provides more energy than the charging step consumes. Based on the electrodes types, the charge and discharge cycles may operate in respect to cell voltages either in steps that are always positive (i), in steps that alternate between positive and negative potentials, crossing the 0 V point (ii), or in steps that are always negative (iii), as seen in Figure 3.

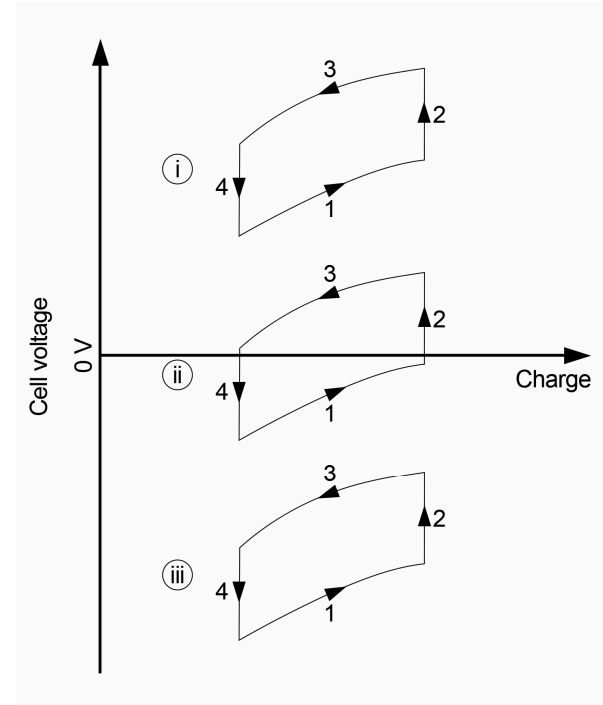


Figure 3. Operating cycles for CapMix under three scenarios in respect to voltage versus charge, where the 1–4 numbers represent the four cycles of the CapMix process.

The CDLE-CapMix cells following the (i) and (iii) cycles require an external energy source during the charging step, providing excess power during discharge as seen in Figure 4. The (ii) cycle, characteristic for CDP-CapMix, is usually achieved by using ionic exchange membranes or electrodes, and does not require an external power source to operate. In this case, both the charge and discharge steps provide power to an external

load, alternating the voltage polarity as seen in Figure 5. If the accumulation of a greater charge is desired, CDP-CapMix may also be operated with an external power source.

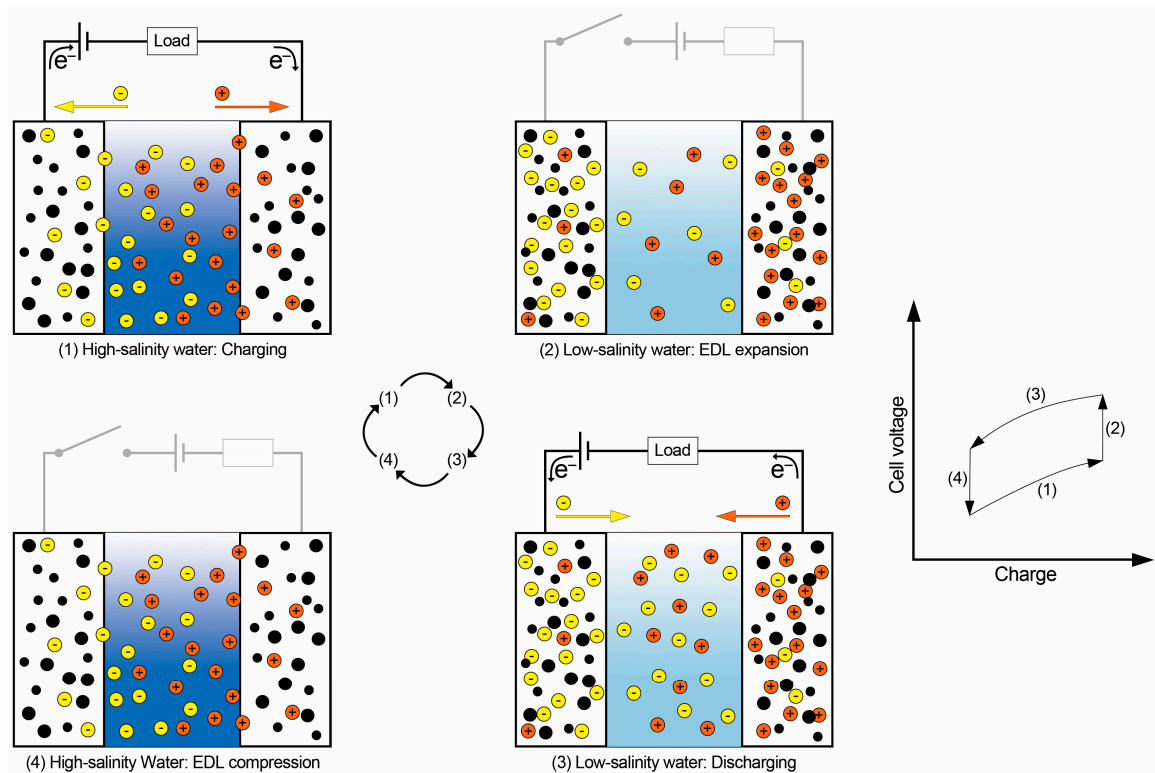


Figure 4. Operating four-step cycle for a CDLE-CapMix cell. The arrows from the external circuit depict the electrons flow directions, modified after [14].

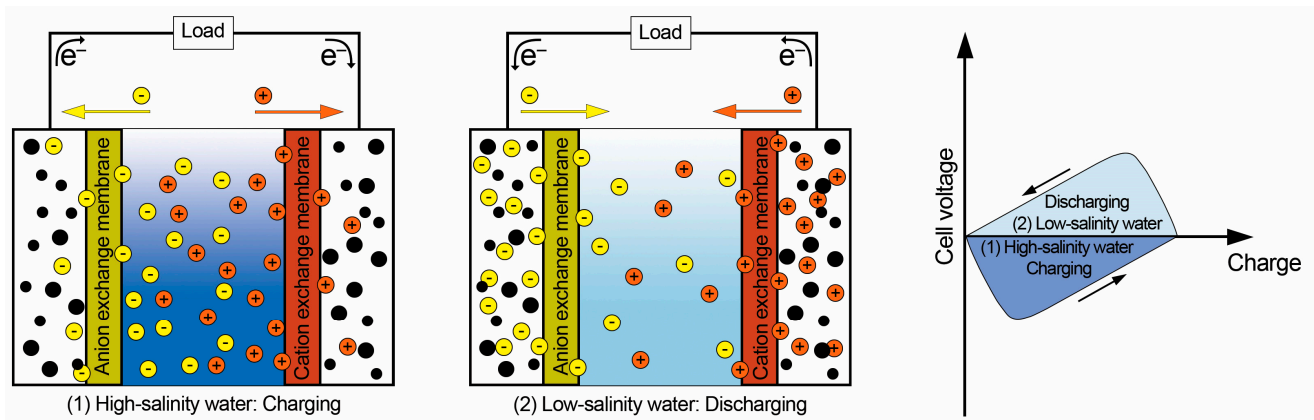


Figure 5. Operating two-step cycle for a CDP-CapMix cell, modified after [14].

In CDLE-CapMix the electric double-layer (EDL) is formed at the contact between the electrode and the electrolyte (salty water) under the external electrical voltage applied during the charge step in HS water. Practically, the applied voltage creates a charge on the surface of the electrodes which leads to the migration of the counter-ions to their respective electrodes. If the voltage difference is below the water splitting or below other ions discharge levels, no electrolysis is performed and the external voltage only creates the EDL with a gap on the order of a fraction of a nanometer. The mechanism in which EDL stores the electric charge is similar to those of an electrical capacitor. Replacing the electrolyte with a lower salinity one, causes the EDL to expand further apart leading to an increase in voltage. This increase in voltage is the one responsible for providing more power during discharge than the power consumed during charge. The electrodes are

usually identical and made from porous activated carbon [32], amorphous coal, graphite or carbon nanotubes [33]. The cell and electrode geometry and type modify the active surface and implicitly the cell's energy extraction efficiency [34]. One of the limitations of this type of CDLE-CapMix is posed by secondary redox reactions that cause charge leakage or self-discharge of the EDL. An improvement of the CDLE-CapMix with identical electrodes is the use of electrodes with different spontaneous potentials. The use of modified electrode pairs, one electrode with negatively charged molecules and the other one with positively charged molecules, reduce the need to use an external power source to maintain the EDL against secondary redox leakage.

In CDP-CapMix, the carbon electrode pair are covered by ion exchange membranes, one with AEM, the other with CEM. The specific affinity of the membranes for their respective ions allows, when they are immersed in HS water, to generate an electrical current as the specific ions are attracted and migrate toward the porous carbon electrodes. After the electrolyte is changed with LS water, the ions migration is reversed toward the electrolyte (also reversing the electrons flow direction in the external circuit).

Other promising directions for the CapMix process include the development of mixing entropy batteries based on pairs of electrodes made from different materials, capable to chemically exchange sodium and chloride ions with the HS and LS electrolytes. Various electrode materials are proposed, such as a sodium manganese oxide electrode (for Na⁺ capture) coupled with a silver chloride electrode (for Cl⁻ capture), or a Prussian blue analogues electrodes (for Na⁺ capture) coupled with a poly-pyrrole electrode (for Cl⁻ capture), or a copper hexacyanoferrate electrode (for Na⁺ capture) [35–37].

3. Pilot Centers for the Generation of Blue Energy

The world's first osmotic power plant with a capacity of 4 kW was opened by Statkraft in 2009 in Tofte, Norway. This plant is able to produce a power density of 1 W/m² of membrane which is obtained at a 10 L/s water flow at a pressure of 10 bar [38].

In Japan, the Mega-ton Water Project was carried out during the years 2010–2013 and focused also on PRO to reduce both the energy consumption and the environmental impact of seawater RO desalination plants [39].

The pilot plant in Afsluitdijk, Netherlands, opened in 2014 to produce 50 kW/h of blue energy and shows technical feasibility under real-life conditions using fresh water from the IJsselmeer and saltwater from the Wadden Sea [40].

The REAPower project developed in the EU used a concentrated brine and sea water as the two different salinity feeds for a RED pilot in Italy. Power densities of up to 11 W/m² were achieved.

4. The Potential Applicability of Salinity Gradient in Romania

The dissolution of sodium chloride from massive salt deposits or from impregnations inevitably leads to an increase in the degree of mineralization of the rivers and streams that flow through or originate from the area of development of Miocene formations containing salt from Romania. Practically, the mineralization process starts from the numerous salty springs that exist in the Carpathian area and at which the highest concentrations of salts (often over 300 g/L) are reached. These springs lead to a rapid increase in the degree of mineralization of the streams that originate in the respective springs or contribute to the mineralization of streams or rivers in the basins they evolve in. For these elements of the hydrographic network, the average mineralization values are usually between 10 and 60–70 g/L. Their gradual collection in rivers with larger flows leads to an increase in the degree of mineralization of those rivers, so that in regions located in the lower course of these rivers, values of 1–5 g/L salt content can be reached, which is quite high for rivers with high flows. However, the degree of mineralization of the rivers also adds to the contribution of the solutions discharged through human activities, which are entirely subordinate, quantitatively.

In the salt rich area in the northeastern part of the Romanian Plain, the streams of several rivers with different degrees of mineralization accumulate, among which the Râmnicul Sărat, Slănicul de Buzău, Ialomița, Putna, Râmna, and Siret should be mentioned. From the above-mentioned rivers, Râmnicul Sărat stands out, sometimes equaled only by Ialomița, to which Buzău is added due to its generally highly mineralized tributary, namely Slănicul de Buzău. In the Transylvanian Basin, Târnava Mică, Someșul Mare, and Olt River stand out from this point of view.

Romania has a significant and untapped potential energy resource based on the salinity gradient, especially considering the discharge of the Danube River into the Black Sea [25].

The Black Sea is extremely valuable from various perspectives: economic, political, social, environmental, and strategic. Blue growth and blue energy should play a more important role in the projections and initiatives of the European Union for all maritime basins within its scope, especially that of the Black Sea [41].

Romania is rich in salt deposits and has also many salt and brackish water lakes, of various size and origin (Table 2).

Table 2. Hydro-chemical data of some brackish, salt and hypersaline Romanian lakes [42–44].

Lake Name	County	Area (km ²)	Depth (m)	Conc. (g/L)	Year	Water Class Type	Cation Group	Origin
Căldărușani	Ilfov	2.24	4.0	0.52	1956	bicarbonatic	Na	fluviatile liman
Balta Maia	Ialomița	0.2	-	0.70	1954	bicarbonatic	Ca	fluviatile liman
Fundata	Ialomița	5	-	12.64	1956	sulfatic	Na	fluviatile liman
Reviga	Ialomița	-	-	5.73	1956	bicarbonatic	Na	fluviatile liman
Schiauca	Ialomița	1.0	-	5.73	1956	chloridic	Na	fluviatile liman
Amara-Slobozia	Ialomița	1.32	3.0	20.06	1956	chloridic	Na	fluviatile liman
Iezer-Ialomița	Ialomița	1.42	-	2.07	1956	chloridic	Na	fluviatile liman
Strachina	Ialomița	5.64	-	9.15	1957	chloridic	Na	fluviatile liman
Balta Amara	Buzău	6.98	-	7.93	1957		Na	fluviatile liman
Balta Albă	Buzău	10.68	-	1.07	1957	bicarbonatic	Na	fluviatile liman
Balta Jirlău	Brăila	10.68	-	3.11	1956	bicarbonatic	Na	fluviatile liman
Ciineni (Sărat)	Brăila	0.56	-	29.25	1957	chloridic	Na	fluviatile liman
Batogu	Brăila	1.31 *	-	59.13	1957	chloridic	Na	karsto-klastic
Chioibășești	Brăila	1.18 *	-	9.04		sulfatic	Na	karsto-klastic
Plașcu	Brăila	1.88	-	8.58		sulfatic	Na	karsto-klastic
Tătaru	Brăila	3.28	-	12.50		sulfatic	Na	karsto-klastic
Ianca	Brăila	3.32	-	34.46		chloridic	Na	karsto-klastic
Plopul	Brăila	1.80	-	18.89		chloridic	Na	karsto-klastic
Movila Miresii	Brăila	1.80	-	137.97		chloridic	Na	karsto-klastic
Lutu Alb	Brăila	3.1 3.45 *	-	21.58		chloridic	Na	karsto-klastic
Lacul Sărat-Brăila	Brăila	1.72	-	83.96	1956	sulfatic	Na	karsto-klastic
Balta Filipești-Târg	Prahova	0.02 *	-	0.72	1955	bicarbonatic	Ca	floodplain lake

Table 2. Cont.

Lake Name	County	Area (km ²)	Depth (m)	Conc. (g/L)	Year	Water Class Type	Cation Group	Origin
Balta Tălăbasca	Galați	1.44	-	0.82	1953	bicarbonatic	Ca	floodplain lake
Balta Mălina	Galați	0.8 *	-	0.72	1953	bicarbonatic	Ca	floodplain lake
Balta Cătușa	Galați	0.42 *	-	0.61	1953	bicarbonatic	Ca	floodplain lake
Viișoara	Botoșani	0.55 *	-	17.60	1956	chloridic	Na	pond
Balta Suhaia	Teleorman	31.20	-	0.92		bicarbonatic	Na	floodplain lake
Babadag	Tulcea	22.52	-	1.76	1957	chloridic	Na	fluviatile-maritime liman
Razelm (at Sarinasuf)	Tulcea	393.30	3.0	1.03	1956	chloridic	Na	sea lagoon
Razelm (at Jurilovca)	Tulcea			2.52	1957	chloridic	Na	
Duingi (Histria)	Tulcea	3.76 *	-	36.99	1954	chloridic	Na	sea lagoon
Tăbăcăriei	Constanța	1.10	-	0.80	1957	bicarbonatic	Na	sea lagoon
Siutghiol	Constanța	21.05	18.0	0.75	1957	bicarbonatic	Na	sea lagoon
Taşaul	Constanța	18.30	5.6	1.85	1957	chloridic	Na	fluviatile-maritime liman
Gargalic (Corbu)	Constanța	3.10	-	2.97	1957	chloridic	Na	fluviatile-maritime liman
Techirghiol	Constanța	10.68	9.0	95.52	1953	chloridic	Na	fluviatile-maritime liman
Mangalia	Constanța	2.6	-	1.29	1949	chloridic	Na	fluviatile-maritime liman
Lacu Sărat Ocelele Mari	Vâlcea	0.02 *	-	262.13	1954	chloridic	Na	karsto-saline
Stelei-Țintea	Prahova	0.005 *	-	79.11	1955	chloridic	Na	karsto-saline
Sărat-Telega	Prahova	0.004 * for all	-	117.73	1955	chloridic	Na	karsto-saline
Ursu-Sovata	Mureș	0.038	18.9	256.70	1953	chloridic	Na	karsto-saline
Aluniș-Sovata	Mureș	0.003	7.4	77.76	1954	chloridic	Na	karsto-saline
Șerpilor-Sovata	Mureș	-	-	232.65	1954	chloridic	Na	karsto-saline
Roșu-Sovata	Mureș	0.001	2.5	233.82	1954	chloridic	Na	karsto-saline
Ocnița-Ocna Sibiului	Sibiu	-	-	230.19	1953	chloridic	Na	karsto-saline
Roman-Turda	Cluj	-	7	77.78	1951	chloridic	Na	karsto-saline
Geaca	Cluj	0.55 Cătina 1.63 Țaga	2.89 Cătina 3.00 Țaga	0.72 Geaca	1953	bicarbonatic	Ca	pond
Zaul-de-Cîmpie	Mureș	1.17	1.95	1.78	1955	bicarbonatic	Ca	pond
Iazul Paharnicul	Iași	Presently dried	-	0.91	1959	bicarbonatic	Ca	pond
Știucilor	Cluj	0.80	12.0	1.02	1958	bicarbonatic	Ca	pond

Table 2. Cont.

Lake Name	County	Area (km ²)	Depth (m)	Conc. (g/L)	Year	Water Class Type	Cation Group	Origin
Sărăturile I (Murighiol)	Tulcea	0.2	2.60	36.11	1960	chloridic	Na	mixed **
Sărăturile II (Murighiol)	Tulcea	-		28.41	1960	chloridic	Na	mixed **
Sărat-Greci	Tulcea	Presently dried	-	3.03	1960	chloridic	Na	fluviatile liman
Tătlăgeac	Constanța	0.84	-	0.79	1960	chloridic	Mg	fluviatile-maritime liman

Note(s): * measured on Google Earth; ** mixed: karsto-klastic, floodplain lake and by aeolian damming processes [45,46].

Salt waters are defined as those waters having a concentration of dissolved mineral salts (salinity) between 30 and 40 g/L, while brackish waters have the mineral salts concentration between 0.5 and 30 g/L, and “fresh” waters less than 0.5 g/L [47]. For the sea water an average value of 35 g/L is used in calculations, but the salinity varies with the fresh water intake, precipitation amount, water currents, as well as with the season and climate zone. Due to these conditions, the salinity of the Black Sea varies between 17 and 21 g/L, even lower values being found in proximity of the Danube River discharge mouths. Hypersaline waters (brines), containing more than 40 g/L dissolved salts, and brine lakes are found, in Romania, located on old salt exploitations, whose ceilings collapsed.

Another classification took into consideration the limit of 1 g/L for fresh water (based on the perception of salty taste by humans), 1–25 g/L for brackish water, 30–50 g/L for the lakes with marine salinity and over 50 g/L for brines. Concentrations higher than 50 g/L were not found in the sea water [42,43].

Depending on the dominant anion, there are three types of lake waters: bicarbonatic, sulfatic and chloridic. Depending on the dominant cations, in each water type there can be three groups: Ca, Mg, and Na.

Table 2 shows the main properties of natural and man-made (ponds) lakes with brackish, salt and hypersaline water in Romania, information adapted from various authors [42–44]. All of the water bodies presence and state were checked on Google Earth time series images.

Natural lakes with brackish waters are found in areas with low humidity, where the water evaporation is higher and the precipitations lower than in the other areas.

They can have various origins (Figure 6) and are located in the:

- Danube River floodplain, near Zimnicea (Balta Suhaia);
- Prahova River catchment (Balta Filipești-Târg);
- Ialomița River catchment (Căldărușani, Balta Maia, Fundata, Reviga, Șchiauca, Amara—Slobozia, Iezer, Stachina);
- Buzău River catchment (Balta Amara—Buzău, Balta Albă, Jirlău);
- Padina Plain, near Făurei (Choibășești or Chichinețu, Plașcu, Tătaru);
- Brăila Plain (Plopu, Lutu Alb);
- Siret River Catchment (Balta Tălăbasca, Balta Mălina, Balta Cătușa);
- Prut River catchment (Vișoara);
- Dobrogea region (Babadag, Razelm complex, Tașaul, Gargalic, Mangalia, Sărat-Greci, Tătlăgeac).

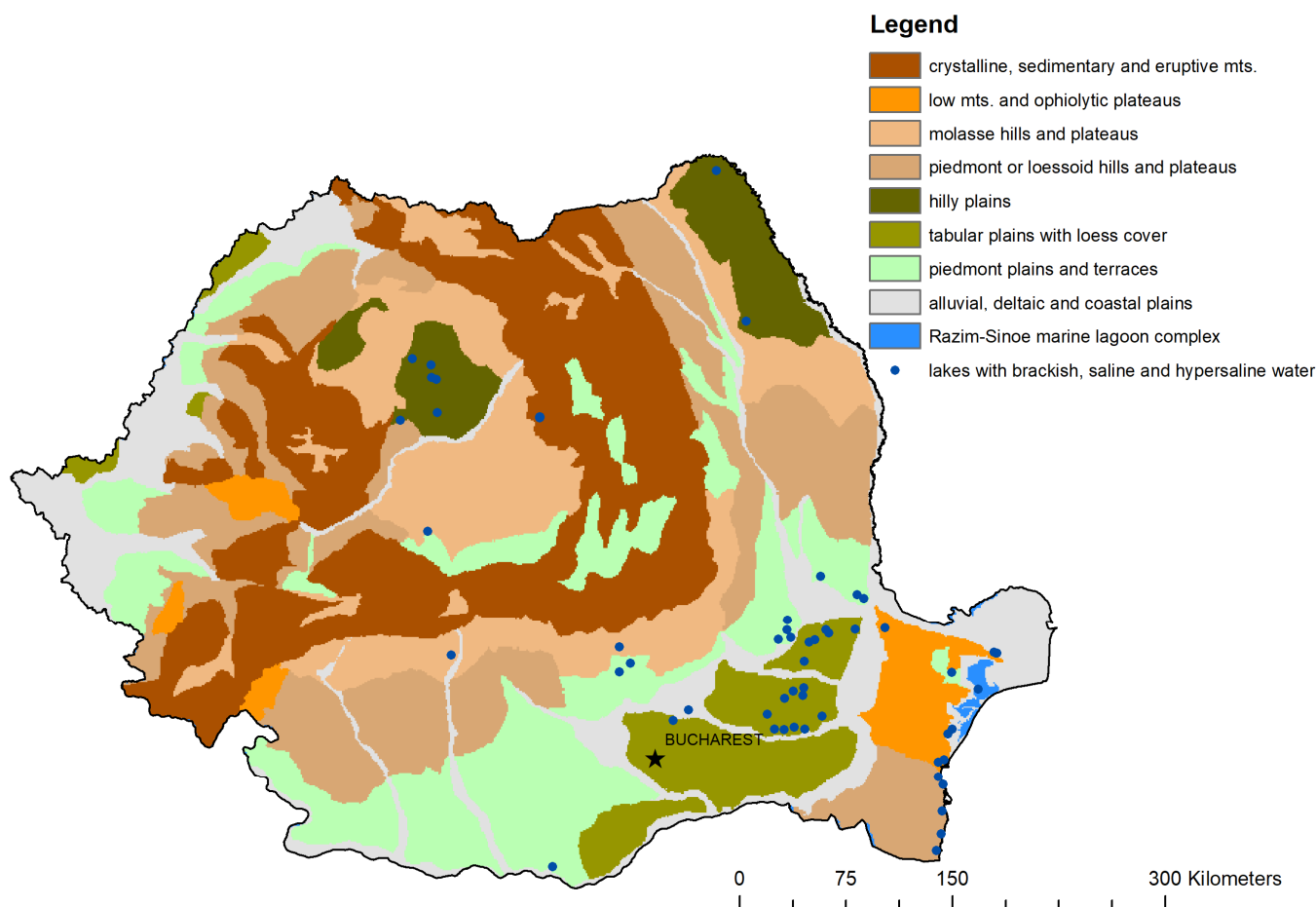


Figure 6. Lakes with brackish, saline and hypersaline waters in Romania marked on a simplified map of geomorphological types.

Man-made lakes (ponds) were mentioned on maps and old documents dating as far as 15th century. By damming the natural course of a river, people had increased the water supplies to be used in arid areas (many were found in the Moldavian Plateau, but they were present also, to a smaller extent, in the Transylvania Plateau) or for fish farms.

Salt lakes were found in the Romanian Plain (Movila Miresii, Ianca, Batogu, Lacu Sărat—Brăila), on the Black Sea shore (Histria or Duingi, Techirghiol), and in a great number in the Transylvania Plateau and Sub-Carpathians, in the areas of old salt mines (Ocnele Mari, Ocna Sibiului, Ocna Dej, Turda, etc.). The concentration in dissolved salts was less than 100 g/L in natural lakes located in areas with scarce humidity in the Eastern part of the Romanian Plain, which were formed by suffusion processes in loessoid deposits. In the lakes formed in or in the proximity of old salt mines the concentration was very high, close to saturation [42]. The concentration of salt lakes changes during the year depending on the hydrometeorological conditions.

Many of the salt lakes formed in relation with salt diapirs are used in balneology and some have also sapropelic mud. Figure 7 exemplifies the use of small hypersaline lakes in balneology, at Ocna Sibiului from the Transylvania Plateau.



Figure 7. Balneology use for the hypersaline lakes at Ocna Sibiului [48].

Installing a PRO or RED plant in Romania could prove challenging due to the need of obtaining a license. Although there are numerous salt and brine lakes in the country, any proposed installation must ensure that the activities, such as balneology, and the equilibrium of the salt water body are not disturbed or negatively impacted. Furthermore, studies have shown [49] that the efficiency of running a power-generating installation based on SGP required the availability of some hundreds of m^3/day of water as an input in the plant. We consider, therefore, that regarding the water flow, a prospective site would be on the dam of Sulina, which is advancing around 4 km into the sea, and where the fresh waters of the Danube River are mixing with the waters of the Black Sea. Another envisaged location could be on the shores of the Danube River Canal at Agigea or Năvodari.

Estimation of the Theoretical Amount of Energy Released When Mixing Water Streams with Different Salinity

The theoretical potential obtained from the Gibbs free energy balance between the input of concentrated and diluted streams and the resulting brackish effluent represents the maximum available energy considering an ideal extraction:

$$TP = (G_c + G_d) - G_b$$

$$G_i = T_i \cdot Q_i \cdot m_i \cdot R \cdot [x_i \cdot \ln(x_i) + y_i \cdot \ln(y_i)]$$

where TP is the theoretical available potential energy (W), G is the Gibbs free energy (W) for the concentrated, diluted and brackish streams (c, d, b), T is the absolute temperature (K)

of the respective stream, Q is the flow-rate ($\text{m}^3 \cdot \text{s}^{-1}$), m is the total number of moles (anions, cations and water) per unit of volume ($\text{mol} \cdot \text{m}^{-3}$), R is the universal gas constant ($8314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), x is the sum of the molar fractions of the corresponding anions and cations, y is the molar fraction of the water content [9].

Taking into account technological performance limitations and environmental restraints, only a fraction of this TP may be achieved. Other works detail the estimation algorithms of various constraints on the available TP [9]. As such, after considering the limitation of water extraction at river mouths due to environmental reasons (such as maintaining the minimum ecological flow), only about 20% of TP remains available. Further considering the natural variability of the river's characteristics, only about 16.8% of TP remains available. After also factoring in the technological restraints and efficiencies, a better estimation of achievable power (AP) generation at river mouths of about 3.14% of the original TP is expected. These are all general assumptions useful for an initial assessment and comparison of different potential freshwater and saltwater sources. Further in-depth investigations are needed to confirm the AP of particular cases, since each particular case may pose additional restrictions or allotments and the specific selected technology may yield other efficiencies.

Table 3 presents the TP and AP for the main discharge pathways of the Danube River into the Black Sea. Sulina and Sf. Gheorghe branches have mouths on the Romanian coast to the Black Sea while the Chilia branch, also being a national border between Romania and Ukraine, has its main mouth on the Ukraine coast to the Black Sea.

Table 3. The TP and AP for the main discharge pathways of the Danube River into the Black Sea.

River Pathway	Average Flow ($\text{m}^3 \cdot \text{s}^{-1}$)	TP (MW)	AP (MW)
Danube—upstream branching into its Delta	5900	3100	100
Chilia Branch	3000	1600	50
Sf. Gheorghe Branch	1800	950	30
Sulina Branch	1200	650	20

The values in Table 3 were determined based on the Danube's average flow-rate between 2014–2018 [50].

The Black Sea salinity near the Romanian coastline varies as a result of the freshwaters discharged by the Danube (Figure 8). In the northern region, influenced by the Chilia branch discharge, the salinity has values of around 6‰. The salinity increases towards 15‰ at Constanța and towards 20‰ at Vama Veche. For the estimation of TP, a salinity of around 10‰ was assumed. An increase in AP might be achieved by selecting a sea water extraction point to take advantage of the Black Sea stratification which may provide waters with higher salinities at depths greater than 120 m. Further assessment is needed to estimate if the increase in salinity will provide more AP than the supplemental power required for pumping water with higher salinity from greater depths.

The results of this present study may be useful for further research regarding public policies for the development of renewable energy. Furthermore, it provides a useful analysis in order to encourage future potential renewables energy investments in Romania.



Figure 8. Danube River discharge toward the Black Sea [51].

5. Conclusions

“Blue Energy” is a promising renewable energy source for the future. If properly designed and adapted to the applied area, Pressure Retarded Osmosis (PRO), Reversed Electrodialysis (RED), and Capacitive Mixing (CAPMIX) represent sustainable energy technologies. By exploiting salinity gradients, the efficiency of the use of renewable natural resources increases, the environment is better preserved and protected, and the specific technologies keep a low-carbon footprint.

Although the potential of salinity gradient energy has been recognized for over half a century, its use has not been considered economically feasible at present.

Membrane fouling processes affect energy profitability, and the extent of this phenomenon depends on several factors, such as salinity levels, water’s ionic and organic constituents, biota, membrane types, cells geometry, exploitation regime, feed water pre-treatment steps, and so on. Stable technological configurations must be established through long-term testing under simulated in situ conditions.

Romania has significant potential for blue energy resources, both for large capacity installations (Danube River-Black Sea) and for smaller capacity devices located around saline lakes and salt deposits.

Romania’s potential for salinity gradient energy should be further explored, as it can provide a sustainable source of renewable energy. The development of this energy source could contribute to the country’s economic growth and reduce its dependence on fossil fuels. Additionally, the utilization of this resource can contribute to the EU’s blue growth and blue energy initiatives, especially in the Black Sea basin.

Further research and investment in salinity gradient energy technologies are needed to fully realize its potential in Romania. This can involve collaboration between government agencies, academic institutions, and private industry to develop efficient and cost-effective methods for energy production.

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