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Salinity gradient power using in the Black Sea regions (in frame of the blue growth development)

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ABSTRACT

Problem Statement. Today, humanity is in search of new sources of energy to make the economy more sustainable, as well as the need for a transition to energy that works on the principles of Carbon-Free Technology. For the Black Sea, this is expressed in the desire for successful implementation of the program Blue Growth Accelerator, which is aimed at the introduction of innovative technologies and alternative energy sources in the energy sector of the Black Sea countries, for the development of the "Blue Economy" and the achievement of its healthy, productive and sustainable state. Salinity gradient power (SGP) is one of the new renewable energy sources. The most studied methods for obtaining SGP energy are technologies based on: Reverse Electrodialysis and Pressure Retarded Osmosis. The interaction of fresh and salt water can provide, in fact, unlimited, free and clean energy. The basis for the generation of such energy is the so-called salinity gradient that occurs when two types of water are mixed. After decades of work and numerous experiments, scientists have developed a way to use the energy of the salinity gradient to generate electricity. This type of electricity is also called "Blue Energy" by association with the color of mixing freshwater and salt water when rivers flow into the ocean. Places (estuaries or deltas), where rivers flow into the oceans and seas, have a truly enormous energy potential.

The aim of this study is to identify sites in the northwestern Black Sea region with the necessary conditions for the development of Salinity Gradient Power energy, as well as to assess their potential using the example of estimating the maximum theoretical power of the Pressure Retarded Osmosis process.

Research Methodology. In a PRO system, the less concentrated solution flows towards the more concentrated solution due to the positive osmotic pressure difference as long as this difference remains greater than the hydrostatic pressure difference. It is by this principle that osmotic power is produced. Theoretically available amount of energy released when mixing 1 m^3 of saturated brine (5 mol/l NaCl solution) and 1 m^3 of sea water (0.5 mol/l NaCl) at 293 K is 10 MJ. In the northwestern Black Sea region, along the coast between the Danube and Dnieper rivers, there are 21 limans (lagoons) of which some can be used to generate of Salinity Gradient Power.

Results. The results of calculating the maximum net power showed that highest values obtained in the summer months, when the salinity in limans reaches its maximum and, consequently, its difference with the salinity of sea (river) water increases. Proceeding from maximum net power, obtained for the Western Sivash, where the salinity is maintained artificially at certain values, it can be seen that the annual amplitude has a smaller value, which provides more stable conditions. There are objects in the northwestern Black Sea region, in the waters of which, as soon as technologies become available, it will be possible to implement SGP projects. The Kuialnyk Liman, Sasyk- Sivash lake and Western Sivash have the most favorable conditions, where the highest power indicators are shown when using the sea water – hypersaline solution scheme, in which freshwater is not consumed.

Keywords: *Salinity Gradient Power, Reverse Electrodialysis, Pressure Retarded Osmosis, northwestern Black Sea region, Black Sea, Blue Growth, renewable energy.*

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Introduction. Today, humanity is in search of new sources of energy to make the economy more sustainable, as well as the need for a transition to energy that works on the principles of Carbon-Free Technology. For the Black Sea, this is expressed in the desire for successful implementation of the program Blue Growth Accelerator, which is aimed at the introduction of innovative technologies and alternative energy sources in the energy sector of the Black Sea countries, for the development of the "Blue Economy" and the achievement of its healthy, productive and sustainable state.

The interaction of fresh and salt water can provide, in fact, unlimited, free and clean energy. The basis for the generation of such energy is the so-called salinity gradient that occurs when two types of water are mixed. After decades of work and numerous experiments, scientists have developed a way to use the energy of the salinity gradient to generate electricity. This type of electricity is also called "Blue

Energy" by association with the color of mixing freshwater and salt water when rivers flow into the ocean. Places (estuaries or deltas), where rivers flow into the oceans and seas, have a truly enormous energy potential.

Salinity gradient power (SGP) is one of the new renewable energy sources. The most studied methods for obtaining SGP energy are technologies based on:

1. Reverse Electrodialysis (RED),
2. Pressure Retarded Osmosis (PRO).

Academic research, mostly done in laboratories, shows that SGP energy has a huge theoretical potential of ~1.9 TW (theoretical potential is the energy that is potentially available if all the energy dissipated in estuaries is used without any energy loss). However, the technical potential (energy that can be extracted with modern technologies, regardless of other limitations) is about 60 % of the theoretical potential and is about 980 GW [1]. In addition, the final energy output depends on local conditions, which may impose restrictions on its production, which must be taken into account when designing SGP power plants [2].

The aim of this study is to identify sites in the northwestern Black Sea region with the necessary conditions for the development of Salinity Gradient Power (SGP) energy, as well as to assess their potential using the example of estimating the maximum theoretical power of the Pressure Retarded Osmosis process.

Working principle of SGP systems. The main approach to obtain salinity gradient energy is energy conversion, which occurs when controlled mixing (using selective membranes) of two solutions with different salt concentrations. The use of selective membranes means that mixing is limited to one of the components: either solvent (water) or solutes (dissolved salts). In the literature, several methods have been proposed for converting the energy of a salinity gradient based on the use of water-permeable membranes as in pressure-retarded osmosis [3], or based on the use of ion-selective membranes as in reverse electrodialysis [4].

Reverse Electrodialysis (RED). Direct electrodialysis has already been used quite successfully in desalination plants. Electrodialysis is a membrane separation process in which solute ions are transported across a membrane by the action of an electric field. The driving force of the process is the electric potential gradient.

Reverse electrodialysis requires two types of selective membranes: membranes that are transparent only to positive salt ions (sodium ions), and membranes that allow only negative ions to pass through (chloride ions) [5].

In a reverse electrodialysis system for power generation from a salinity gradient, as in direct electrodialysis, several cells are located between the cathode and anode, separated by membranes. The compartments between the membranes are alternately filled with a concentrated salt solution and a dilute salt solution. The salinity gradient results in a potential difference (e.g. 80-100 mV for sea water and river water) over each membrane, the so-called membrane potential. The electrical potential difference between the outer compartments of the membrane package is the sum of the potential differences across each membrane. The difference in chemical potentials causes the transfer of ions through membranes from the concentrated solution to the diluted solution. For a sodium chloride solution, sodium ions permeate through the cation-exchange membrane in the direction of the cathode, and chloride ions permeate through the anion-exchange membrane in the direction of the anode. Electro-neutrality of the solutions in both the anode compartment and cathode compartment is maintained through redox reactions at the electrodes. As a result, electrons can be transferred from anode to cathode via an external electric circuit (Fig. 1). This electrical current and the potential difference over the electrodes can be used to generate

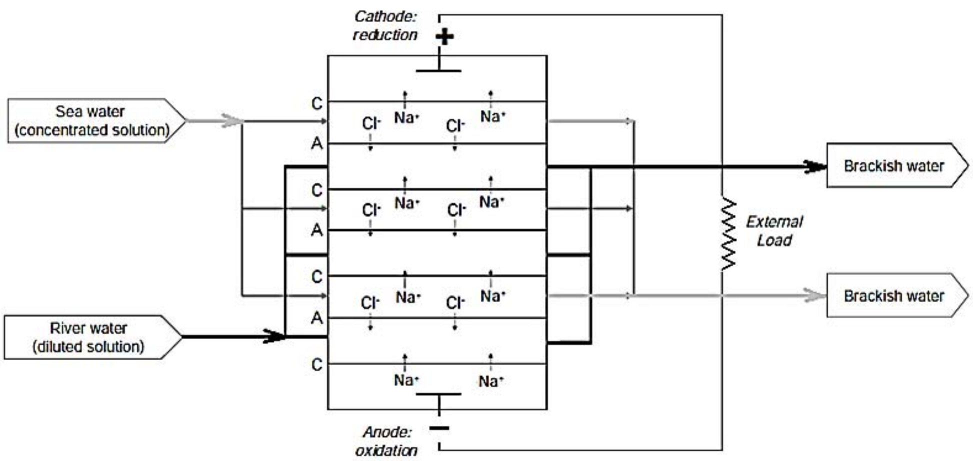

Fig. 1. Conceptual scheme of salinity-gradient energy produced by reverse electrodialysis (C is cation-exchange membrane, A is anion-exchange membrane)

electrical power, when an external load or energy consumer (e.g., a light bulb) is included in the circuit [4].

Pressure Retarded Osmosis (PRO). The energy released by mixing fresh and salt water can be easily used. This is explained by the effect of osmosis, hence the name "osmotic energy". Osmosis is the transport of water across a semi-permeable membrane from a solution with a higher chemical potential (i.e. lower osmotic pressure or lower salt concentration) it's usually called "feed solution" to a solution with a lower chemical potential (i.e. higher osmotic pressure or higher salt concentration) – called "draw solution". This semi-permeable membrane allows the feed solution to pass by discarding solute molecules or ions.

If we separate two solutions with different concentrations by a semi-permeable partition (membrane) that allows molecules of feed solution to pass through, but preventing the transition of particles of draw solution, there will be a spontaneous transition (the system spontaneously tends to move into a prefect mixture) feed solution through the membrane from feed solution into a more concentrated draw solution. To achieve the maximum value of the entropy of the system, salt ions tend to be evenly distributed throughout the volume of the solution. As a result of the diffusion water molecules from dilute solution (A) into concentration solution (B), the total volume of the B will increase and the level rises until a specific pressure head is reached which counteracts the diffusion of the water molecules from A into B. This pressure is called osmotic pressure π of the solution B.

The osmotic properties of a solution are quantitatively characterized by the value of the osmotic pressure. Osmotic pressure is the pressure that a feed solution exerts on a semi-permeable membrane when moving from an area with a lower concentration of solute to an area of higher concentration.

In a PRO system (Fig. 2), the less concentrated solution flows towards the more concentrated solution due to the positive osmotic pressure difference as long as this difference remains greater than the hydrostatic pressure difference ΔP. It is by this principle that osmotic power is produced. For stable energy production, the salt water side must be maintained at a constant pressure and concentration while the feed solution provides a constant flow through the membranes, increasing the volume flow on the salt water side.

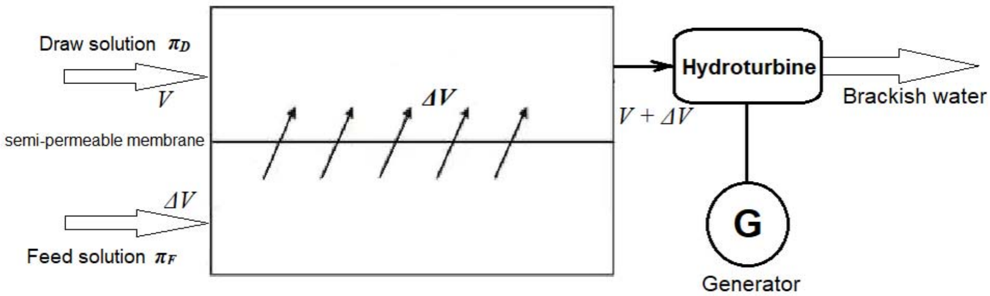

Fig. 2. Conceptual scheme of salinity-gradient energy produced by pressure-retarded osmosis process

The transport of water from the low-pressure diluted solution to the high-pressure concentrated solution results in a pressurization of the volume of transported water. The volume of pressurized water transported can be used to generate electrical power in a turbine [4]. It is known from experience that the pressure head between 0.5 molar seawater (equivalent to 30 ‰ salinity) and fresh water (river water) is about 24 atm [6]. This pressure is equivalent to a 240 m water head.

An assessment method of the net maximum theoretical power in PRO process. PRO process and osmotic power calculation method are described in more detail in [7, 8]. We will only give the basic equations with which we calculated the maximum theoretical power. As mentioned in 1, the main driving force in PRO systems is the difference in osmotic pressure in solutions of different concentrations separated by a membrane. The osmotic pressure π of any solution can be calculated using the van't Hoff equation

$$\pi = icRT \quad (1)$$

where c – the molar concentration ($mol \cdot L^{-1}$), R – the universal gas constant (8,31441 $N \cdot m \cdot mol^{-1} \cdot K^{-1}$), T – the absolute temperature (K), i – the number of osmotically active particles in the solution, equal

$$i = 1 + \alpha(\nu - 1),$$

where α – the degree of dissociation, ν – the stoichiometric coefficient of dissociation reaction (for NaCl α = 1 and ν = 2, thus i = 2).

The resulting unit for π in the equation (1) is kPa. For example, for sea water, where the concentration NaCl is 30-40 ‰ (or approximately 30-40 $g \cdot L^{-1}$, or from 0,51 to 0,68 $mol \cdot L^{-1}$), osmotic pressure is between 25 and 33 bar at a temperature 25 °C.

The potential flux through the membrane is calculated as a function of the difference in osmotic pressure between the two solutions (Δπ, in bar), the difference of hydrostatic pressure (ΔP, in bar),) and the intrinsic water permeability coefficient of the membrane (A, typically in $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)

$$J = A(\Delta\pi - \Delta P) \quad (2)$$

where J − the water flux (typically in $L \cdot m^{-2} \cdot h^{-1}$), $\Delta\pi = \pi_D - \pi_F$, where π_D − the osmotic pressure in the draw solution, π_F − the osmotic pressure in the feed solution, $\Delta P = P_D - P_F$, respectively.

A concentrated solution (draw solution) with a volume V and with osmotic pressure π_D is pumped into the installation at hydraulic pressure P_D. The power input is given by the product of the volume flow V and the input hydraulic pressure P_D. At the same time, less concentrated water (feed solution) enters the permeator on the other side of the membrane module at osmotic and hydraulic pressures that are low in comparison to these quantities on the concentrated side. Water permeates the membrane from the less concentrated side to the more concentrated side at a rate ΔV (note $\Delta V = J \cdot Am$, where Am — membrane area and J is the water flux from (2)) and acquires a pressure P_D. The mixture of the feed and draw solutions creates a new solution of brackish water, with much lower osmotic pressure. The brackish water (volume $V + \Delta V$) enters a hydroturbine in which the hydraulic pressure P_D is reduced to zero, as it delivers power of magnitude $P_D (V + \Delta V)$.

The maximum net power (theoretical) W_{net}^{max}, which can be produced according to the ideal PRO scheme, is

$$W_{net}^{max} = P_D(V + \Delta V) - P_D V = P_D \Delta V, \quad (3)$$

where $P_D \cdot \Delta V$ – the net power.

It should be noted that the above scheme is idealized, since this net power is achieved under the condition of no energy losses and 100 % mechanical efficiency for all system components. This scheme also assumes that the feed solution enters the system by gravity.

The ideal operating pressure P_D for maximum power output is half the osmotic pressure $\Delta\pi$ [8]. Therefore, for example, for the river-sea PRO scheme, where the osmotic pressure difference $\Delta\pi$ is about 26 bar, the ideal operating pressure P_D would be 13 bar, and the maximum useful output power – 1,3 MW per 1 $m^3 \cdot s^{-1}$ of water (solution) passing through the membrane.

As can be seen from (3), maximum net theoretical power $P_D \cdot \Delta V$ does not depend on the volume of more salty draw solution V, but depends only on operating pressure P_D and water flow through the membrane J. Considering that $\Delta V = J \cdot Am$, then we can conclude that the power is essentially a function of the type of membrane and the osmotic pressure difference $\Delta\pi$, as shown in the equation (2).

Estimates of performance and cost of SGP systems. Theoretically available amount of energy released when mixing 1 m^3 of sea water (0.5 mol/l NaCl solution) and 1 m^3 of river water (0.01 mol/l NaCl solution) both at a temperature of 293 K is 1.4 MJ. According to estimates [9] made for the Mississippi River, its theoretical energy potential (with an average discharge of over 17,000 m^3/s) is 40 GW at an energy density of 2.3 MJ per m^3 of river water. It is assumed that river water is mixed with "endless" cubic meters of sea water. To estimate the potential in a first approximation this assumption can be justified: the available discharge of river water is indeed a limiting source, while the source of sea water can be considered as infinitely available. However, it is clear that this value is highly theoretical, since it does not take into account the effect of water withdrawal on salinity at the point of withdrawal into the sea, as well as on salinity gradients at the very mouth of the river.

As the concentration of NaCl in water increases, the theoretically available amount of energy increases. So, when mixing 1 m^3 of saturated brine (5 mol/l NaCl solution) and 1 m^3 of sea water (0.5 mol/l NaCl) at 293 K is 10 MJ. An example is the planned replenishment of the Dead Sea with sea water from either the Mediterranean or the Red Sea [10], to compensate of evaporation of 3 million m^3/day (although the mineral content of the Dead Sea is very different from normal sea water). At the same time, an elevation difference of 400 m is supposed to be used to generate hydroelectric power from falling sea water, and a salinity gradient is supposed to be used to generate SGP energy. It is assumed that an energy density is 10 MJ per m^3 of sea water, the energy potential under such conditions of the salinity gradient can be 350 MW, of which, according to, it is technically possible to convert 130 MW into electricity [4].

The greater the salinity gradient of the waters used, the greater the energy produced. So, in [11] salinity of sea and river water was assumed to be constant and equal to 37 g/kg and 0.1 g/kg, respectively. It was shown that with an increase in the salinity of sea water by 1 g/l, the useful power increases by 3.9 %. In the case of an increase in freshwater salinity by 1 g/l, the value of useful power decreases by 15.8 %. Reducing the salinity of sea water by 1 g/l leads to a decrease in useful power by 5.3 %. Also, the release of energy is influenced by the temperature of the water. The higher its value, the more SGP energy is released, so with an increase in temperature of both fresh and salt water by 1 °C, the amount of useful power increases by 0.6 %, while a decrease in temperature by 1 °C will lead to a decrease in energy by 0.6 %.

With an increase in the concentration in a salt solution, the theoretically available amount of energy increases, which can be extracted by mixing solutions. Therefore, in a number of studies [12-15], for the generation of SGP energy, it is proposed to consider preferably the option in which sea water and hypersaline solution are mixed. The source of such a highly concentrated brine can be lake waters with high salinity or saline groundwater, for example, when extracting of coal seam gas, the need to 'de-water' coal seams to depressurise the gas results in large volumes of produced water, which usually has large quantities of salts [16]. A salinity ratio of 30:1 is optimal for energy production using RED [17].

An important element of SGP systems, which affects the productivity and cost of generated energy (both PRO and RED) are membranes. The current value of net power density (which considers the membrane potential, resistance and the power required to pump the water) of membranes is a maximum of 2.7 W/m^2, but recent laboratory experiments have achieved a value of 14.4 W/m^2 (for the PRO process). Changing the cell design can increase the calculated net power density close to 20 W/m^2. However, power density is not the only measure of performance. The design of the entire facility, including the circulation of large quantities of water within the plant, determines its performance [18].

In November 2009 in the Tofte, for the first time in the world a pilot PRO power plant was officially opened by the Norwegian company Statkraft. This project used 2000 m^2 of flatsheet membranes and it technically could produce 10 kW, although the actual production was around 5 kW. In 2014, the project was closed due to the lack of long-term financial support mechanisms from investors. The company continued to study and analyze the results obtained during the operation of the power plant.

Besides Statkraft, today in Canada, Singapore and South Korea realize other initiatives to test autonomous power generation with PRO systems. These projects are in the early stages of development, aiming to scale up installations and power generation [18].

In 2003 in the Netherlands a study of power generation based on RED technology was initiated. In 2005 REDStack with Frisia, a European Salt company, 5 kW RED pilot project was started. Based on this first 5 kW pilot, REDStack and Fujifilm started a follow-up a 50 kW pilot project, located on the sea defense site and major causeway called the 'Afsluitdijk'. Work on the 50 kW pilot project has been completed and was officially opened on 11 October 2013. In the longer-term there are plans up to 200 MW for an extended installation at the same location. Statkraft did not release detailed numbers, but in their projections they aimed to produce electricity at a retail price of 65 to 125 USD per MWh [18].

Studies show that the generation of electricity from 3,000,000 m^3/day ("moderate" consumption) of river water when interacting with sea water based on PRO technology is 22,300 kW [19]. This PRO electricity generation cost data was largely based on data from a power plant in Yuma, Arizona [20], where the unit cost was 1,000 USD per m^3/day.

With the exception of cost estimates for existing projects (which reflect pilot plants), there are few reliable estimates of the cost of energy received based on PRO and RED technologies. Estimates of the cost of a kilowatt-hour of electricity generated from SGP have shown that the price ranges from 0.11 EUR/kWh to 0.22 EUR/kWh, the difference depends on the location; arrives at a range of EUR 0.28/kWh for standalone power generation down to EUR 0.11/kWh for an installation that uses the brine from a desalination plant, or other production processes that emit highly saline waters [18]. The values in Table 1 show several advantages of SGP over other energy sources.

Table 1

Comparison of SGP with other energy sources [2]

	GHGs emissions, gCO_2e/kW·h	**Price of generated electricity, USD/kW·h**	**EROI**	**Availability of renewable sources**	**Efficiency of energy conversion, %**
Photovoltaic	90	0.24	1.6-6.8	Dependent	4-22
Wind	25	0.07	18	Dependent	24-54
Hydro	41	0.05	> 100	Always available	> 90
Geothermal	170	0.07	n/a	Dependent	10-20
Coal	1004	0.042	80	Non-renewable	32-45
Gas	543	0.048	10	Non-renewable	45-53
SGP (RED)	< 10	0.10	7	Always available. But not in non-coastal countries	50-70
SGP (PRO)	< 10	0,065-0,13; with subsidies 0,05-0,06	6-7	Always available. But not in non-coastal countries	40

The main economic barrier is membrane costs, which represent 50-80 % of total capital costs. Among the problems associated with the operation of SGP installations are [18]:

1. *Bio-fouling*. Due to the presence of organic matter in sea water and freshwater, bio-fouling is a major problem for both PRO and RED installations. The reason is the fouling of the membranes, which leads to a decrease in energy production. To date, there is no satisfactory low-cost solution to this problem.

2. *Environmental and ecological aspects*. Close to power plants areas of turbulence or recirculation may occur, which increases the risk to inhabitants. To avoid this, and to reduce this effect at the point of water intake, the design of the installation must be adapted taking into account hydrodynamics.

3. *Sector development and supply systems*. One of the main tasks of the sector is the timely development of specialized infrastructure and equipment. There are currently only a limited number of companies manufacturing specialized membranes and other plant parts such as stacks or modules. For scaling will require a large number of specialized consumables.

Among the advantages the following can be distinguished:

1. *Environmental and ecological aspects.* The impact of SGP plants on the environment is minimal, which ensures the preservation of the estuaries and rivers ecological conditions. In this process does not consume water or salt, and the installations can be located underground or in low buildings. Mono nitrogen oxides (NOX), carbon monoxide (CO) or carbon dioxide (CO_2) emissions are absent, and the installations are not important sources of noise.

In addition, hybrid SGP energy generation processes can be used to recover energy from high salinity waste streams. This can be, for example, brine from desalination or salt extraction, as well as wastewater from sewage treatment plants. Using saline wastewater as a source has important environmental benefits as it dilutes saline wastewater streams simultaneously generating renewable electricity. For example, within the European REApower project, an experiment was developed that later became a pilot project for the generation of electricity using sea water and low salinity wastewater.

In terms of overall commercialization, the technology will greatly benefit from an increase in the number of industrial parties and companies with experience in efficiently scaling up the latest developments. The first steps towards such increased participation have already been taken in a number of pilot projects in Europe, Asia and North America / Canada. This is of course in addition to more public engagement because this technology is not well known [18].

Selection of a site for the location of the SGP plant. Most suitable for placing SGP plant are the river mouths. However, not every river mouth is suitable for this, since river and sea water should be available at a short distance in order to reduce the cost of transporting water and the associated costs. Favorable conditions are stratified river mouths, which have significant vertical salinity gradients due to the penetration of sea water close to the bottom in the estuarine zone. If freshwater and seawater intakes are located in the site of the greatest stratification of the estuary, freshwater can be extracted near the surface, while seawater is taken in the nearest coordinate near the river bottom. This configuration significantly reduces the distance between two water intake points and therefore the energy required to transport water to the power plant. However, finding the zone of maximum stratification is not easy due to the inherent variability of flows at the river mouth.

In the methodology proposed in [11] shown that when assessing of the SGP plant location conditions use data about average salinity along the estuary during the dry season of the average climatic year near the surface and at 10 m depth, on which the salinity profile is built.

As it was said above, an important problem is membrane fouling. Therefore, it is necessary to analyze the content of organic matter in the riverbed.

Then, the costs for the production and transmission of electricity are estimated by calculating the net power of the SGP installation at different points of intake water located in the river estuarine zone. Comparison of the results makes it possible to evaluate the advantages between higher electricity generation when water intakes are distant from each other and the costs associated with pumping water over these distances.

From the point of view of the theoretically available energy that can be extracted by mixing solutions, it is preferable to consider a scheme in which sea water and hypersaline solution are mixed. This gives significant salinity gradients and, consequently, the largest energy released in this case. So, in a number of studies [12-15] large-scale water systems with high salinity gradients are considered. The waters of the Caspian, Mediterranean, Atlantic, Indian oceans, etc., with salinity from < 10 g/l up to 45 g/l, suggested to be mixed with highly saline waters of lakes with salinity of 300-348 g/l, as well as use dried lakes with a salt bottom, which can be a source of a highly concentrated solution when filled with water.

The idea is based on the pumping of sea water into a salt lake and a decrease in the volume of water in the lake due to evaporation, which leads to an increase in the concentration of salts in the water. Then, this hyper-concentrated solution would then be paired with sea water (less concentrated) in a SGP plant. So, according to [13], Lake Torrens (South Australia) could be used as a source of hyperconcentrated salt water for osmotic power generation. The lake's area is 5700 km^2 and it remains dry during almost the entire year. In this region the mean annual rainfall is less than 250 mm, and annual potential evaporation is around 3,500 mm. Kelada [13] proposes to expand the seawater canal, connecting the lake and the Spencer Gulf, located about 80 km south of the southern end of the lake, to a capacity of 1000 m^3/s, to fill the lake with sea water. Calculations show that Lake Torrens can provide brine with a salt concentration of 320 g/l, which can be used as a draw solution in an osmotic power plant when paired with the diverted sea water, with 3.5% salt concentration. Thus, this configuration proposed for Torrens Lake can generate up to 2.6 GW of energy for a seawater flow rate 225 m^3/s.

It should be noted that membranes for use in sea water and hypersaline water circuits are currently a problem. According to She et al. [21], and Kim and Elimelech [22], maximum water fluxes and projected optimum power densities for sea water and hypersaline water schemes are difficult to obtain in a laboratory setting with commercially available membranes due to their inability to withstand high pressures. Loeb [23] already suggested that hypersaline lakes such as the Dead Sea and the Great Salt Lake could be used as sources of draw solution to generate osmotic power if membranes could be manufactured for this purpose.

At the same time, the use of the sea water and hypersaline solution from salt lakes scheme will not affect freshwater resources, unlike the river water and sea water scheme. In addition, energy production will not be limited by the availability of feed solution, because there is a lot and practically unlimited of the sea water. This is different from a freshwater and sea water system, which will require large volumes of freshwater, which is not always available in such quantities, especially in areas with high demand for water, where the resource must be shared with other water users, some of them with a higher priority than electricity generation.

Salinity and temperature regime of the Black Sea and limans of the north-western Black Sea coast. Based on the above conditions and the proposed examples, we will further consider the haline conditions in the Black Sea and coastal water bodies of the northwestern Black Sea region from the point of view of the presence of sufficient values of the salinity gradient.

The salinity field in the Black Sea is formed by the balance of freshwater and water exchange through the Bosporus. The excess of freshwater input with streamflow and precipitation over evaporation leads to a relatively low salt content compared to most marine basins. The surface layer salinity of the Black Sea is on average 17.8 ‰, which is almost half the salinity of the surface waters of the World Ocean. The average salinity throughout the Black Sea in the layer 0-300 m is 20.2 ‰. Specific values of water salinity in the Black Sea are in a fairly wide range from 0 to 37 ‰. Isolated volumes of freshwater in the surface layer are observed near river mouths during flood periods. Highly saline Mediterranean waters (34-37 ‰) penetrate in the sea along the bottom of the Bosphorus Submarine Canyon – a continuation of the Bosphorus Strait [24].

A characteristic feature of the vertical haline structure of the sea is the presence of two haloclines: seasonal in the 0-30 m layer and permanent (main) in the 50-100 m layer. The seasonal halocline is well pronounced in the period from April to September, the maximum vertical salinity gradient gradually deepens during this period from the sea surface to a 20 m depth, the gradient values are on average 0,02-0,05 ‰·m^{-1}, in the northwestern part of the sea can reach 2 ‰·m^{-1}. The maximum vertical gradient in the permanent halocline is located at 50-70 m depths, the gradient values are in the range 0,03-0,06 ‰·m^{-1}, maximums may exceed 0,1 ‰·m^{-1} [24].

The average monthly water temperatures in winter off the northern coast of the Karkinitsky Bay are 0,0-2,0 °C, in the Odessa Bay – 0,9-1,1 °C and near the mouth of the Danube – 0,3-2,2 °C. In late March – early April, the water temperature rises rapidly and reaches a maximum in July – August, when the average monthly temperatures are 20-25 °C [24].

In the northwestern Black Sea region, along the coast between the Danube and Dnieper rivers, there are 21 limans (lagoons) (Fig. 3).

The hydrological regime of the limans of the northwestern Black Sea region is characterized by extremely low water content. Limans, which, due to historical circumstances, are deprived of the possibility of free water exchange with the sea through natural or artificial channels in dry years, can significantly dry out and "salinize". The polyhaline type (salinity 15-45 ‰) includes limans: Big Adzhalyksky (Dafinivsky), Dzhantsheysky, Maly Sasyk, Shagany, Karachaus, Alibey, Hadzhider, Curudiol, Burnas, Tiligulsky, Berezanskyi. To the hyperhaline type (salinity > 45 ‰) relate – Kuialnyk Liman, southern part of Sasyk-Sivash, Sivash. However, salinity in most of the listed limans experiences significant changes during the year, during which salinity decreases to values less than 15 ‰. Some limans may belong to a different type of salinity depending on the water content of the year and the inflow of sea water into their water area.

The main components of the water balance of the northwestern Black Sea region limans are: inflow of surface waters into the reservoir, including the inflow of river waters and overland flow from the adjacent territory; water supply due to precipitation fall-

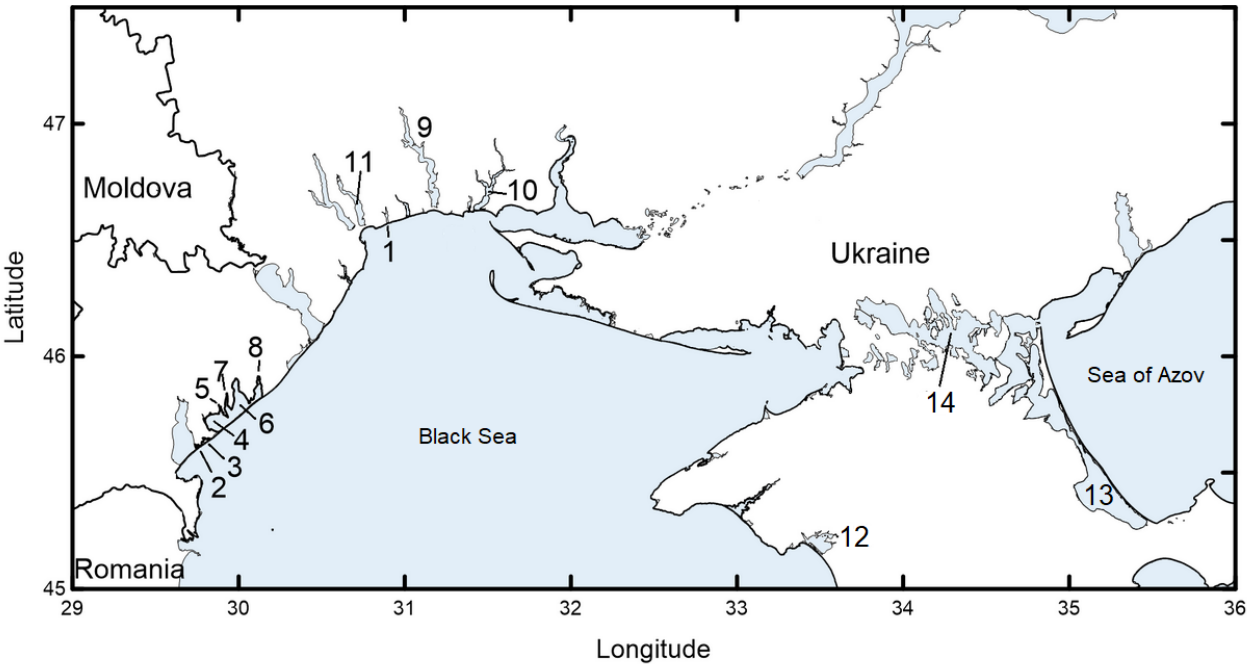

Fig. 3. Polyhaline and hyperhaline limans and reservoirs of the northwestern Black Sea region: 1 – Big Adzhalyksky (Dafinivsky), 2 – Dzhantsheysky, 3 – Maly Sasyk, 4 – Shagany, 5 – Karachaus, 6 – Alibey, 7 – Hadzhider, 8 – Burnas, 9 – Tiligulsky, 10 – Berezanskyi, 11 – Kuialnyk, 12 – Sasyk-Sivash, 13 – eastern part of Sivash, 14 – western part of Sivash

ing on the water surface; water loss due to evaporation; water exchange of limans with the sea; groundwater inflow and water loss for filtration into the banks (in the long-term context, this component of the water balance can be ignored in calculations). The increase in the trend of average annual air temperatures after the 1950s led to an increase in the growth of positive evaporation anomalies.

Results and discussion. Let's consider which water bodies have the necessary characteristics, and which objects can be considered as potentially attractive for the placement of SGP power plants.

As you can see, the salinity of the Black Sea waters does not correspond to the values necessary to use them as a draw solution in SGP installations due to its low salinity (up to 17.0-18.0 ‰ at the surface). Therefore, in this case, it is necessary to look for other sources with a salinity of 30.0-35.0 ‰ and more. Such objects include the following limans:

1. *Shagany Liman* and *Alibey Liman* are part of the Tuzly Limans group, which is located in the south of the Odessa region in the middle part of the Danube-Dniester interfluve. The average area of the Shagany Liman is 71 km^2, and the area of the Alibey Liman is 98 km^2. This complex of connected limans is separated from the sea by a sandbar more than 25 km long. The width of the sandbar ranges from 50 to 400 m, and it height above the water's edge – from 1.5 to 3 m. The water temperature in summer reaches 30 °C, in winter it drops to 0 °C.

The water balance of the group of Tuzly Limans (Fig. 3, number 2 - 8) mainly depends from the characteristics and intensity of water exchange with the sea. In its incoming part, the share of precipitation is 30-40 %, and the inflow of sea water is 60-70 %. The remaining 10 % is the overland flow and the filtration of sea water through the sand bar and partially the outflow of water into the sea through channels during offshore winds. The expenditure component of the Tuzly Limans water balance is mainly represented by evaporation (90-100 %), which can exceed 1000 mm/year, as a result of which the water in the limans becomes saline. In the years when the canals do not work, the water balance of the limans is negative. Model calculations showed [25], that in the average water year during the winter-autumn period the incoming component of the water balance exceeds the outgoing component by 39.1 million m^3. Therefore, when the channels are opened in May, there will be an outflow of liman water into the sea. From June to September, evaporation from the surface of the reservoir is 81.9 million m^3, and the inflow of water due to precipitation (91.1 % of the incoming part of the balance) and overland flow (6.9 %) is only 27.9 million m^3, i.e. water deficit in limans is 44 million m^3.

The salinity of water in limans is subject to significant inter-annual and intra-annual fluctuations. It changes over the years and seasons. In 1868-1869 the Tuzly Limans completely lost contact with the sea, dried up and turned into marshy solonetz soils, which led to an ecological disaster and the almost complete disappearance of water bodies. At the beginning of the 20th century, as a result of the restoration of the connection between the limans and the sea, the salinity of the water decreased. In 1992-1993 in the absence of communication with the sea, the salinity of the limans again increased to 34.0 ‰. Its decrease to 22.0-26.0 ‰ occurred only in 1995 after the opening of two canals for launching fish into the liman from the sea. In 2000, the channels did not work, and salinity already exceeded 26.0-30.0 ‰ in spring, and in autumn 2002, in conditions of complete isolation of limans, it reached 52.5 ‰ [26]. So, according to the results of the expedition in the summer of 2008 [27] in the Shagany Liman, salinity on the water surface was in a wide range, from 45.6 ‰ to 53.1 ‰. The maximum salinity at the bottom was 54.3 ‰, and the minimum was 45.6 ‰. In the Alibey Liman in the surface horizon, the maximum salinity was 54.3 ‰. The average value was 52.4 ‰, which is significantly higher than in the Shagany Liman (47.9 ‰). In the near-bottom horizon of the Alibey Liman, the maximum salinity value coincides with the maximum on the surface and is 54.3 ‰, the minimum is 47.8 ‰. The average salinity at the bottom in Alibey is 52.3 ‰.

In years when the group of Tuzly Limans have a connection with the sea, and the volumes of precipitation and overland flow are quite large, the salinity of the waters decreases. It is always minimal in spring, and maximal in autumn, before the canals open. The recent regime of fishery exploitation of the Tuzly Limans implies the mandatory opening of canals in the spring − for the admission of mullet fry from the sea into the reservoir, and in autumn − for catching mullet in canals when it leaves the limans into the sea. During the summer period (June-September), the estuaries are isolated from the sea to prevent the mullet go to sea. Since water exchange with the open sea through connecting canals in the sandbar, aimed at replenishing the waters of the liman with sea water, plays an important role in stabilizing the hydrological and hydrochemical regime of limans and their ecological state, the intake of saline water for the operation of the SGP plant and the discharge back into the liman of brackish water would help maintain the steady state of the liman.

As a source of freshwater the waters of the Danube River can be used, which is removed from the southwestern shore of the Shagany Liman at a distance of 37 km, and if we take into account the canal connecting the Danube and Sasyk Lake – at a distance of 30 km.

2. *Kuialnyk Liman* is a closed body of water in the northwestern Black Sea region, the inflow of surface water into which is constantly decreasing. Kuialnyk Liman can be attributed to water bodies with extremely high salinity. Its area varies from 25 to 60 km^2, the average depth does not exceed 0.30-1.0 m. The liman is located in the mouth section of the Bolshoy Kuyalnik River and is separated from the sea by a sandbar. The water level in the liman is usually 5 m below the Black Sea level, but it, like the water salinity, changes regularly. In some years, salt precipitates to the bottom of the liman. Recently, due to the regulation of the Bolshoy Kuyalnik River the water area of the Kuialnyk Liman has decreased by almost three times and now is 2,240 km^2.

The hydrological and hydrochemical regime of the Kuialnyk Liman is determined by natural and anthropogenic factors: the Bolshoy Kuyalnik streamflow, inflow of fresh and brackish waters from reservoirs and streams of the liman sandbar and adjacent territories, atmospheric precipitation and evaporation, filtration of sea water through the sandbar, overland flow and groundwater flow, development of hydrobiological processes within the liman. The natural inflow of water into the liman is carried out due to precipitation, overland and groundwater flow, water filtration through the sandbar, wherein the last two components do not reach 1 % of the total inflow [28]. In 2011-2012 according to [29] streamflow was about 2 million m^3/year. The drainage area of the Bolshoy Kuyalnik River is 1780 km^2, and the water area of liman is 450 km^2. Salinity of brine in October in the southern part of the Kuialnyk Liman in 1997-2012 ranged from 112.0 ‰ in 2004 to 319.0 ‰ in 2011. In 2008-2014 the average monthly salinity was 200.0-320.0 ‰, and the absolute values in the summer-autumn period reached 399.9 ‰ in the shallow northern part of the liman [30].

After the completion of the project to restore the Kuialnyk Liman, in which it was connected to the sea by a pipeline (the distance to the sea is about 2 km) [31], since 2014, to restore the water regime of the liman, annually (December–April) about 10 million m^3 of sea water are let in by gravity, as a result, the mineralization of brine in the liman decreased from more than 300.0 ‰ to 240.0 ‰. Together with water, more than 350 thousand tons of salts were brought into the liman [32]. Thus, even the undertaken replenishment of the liman with sea water in the winter-spring (December-April) months of 2014-2016 allowed only to maintain the state of the liman at the level of recent years [33]. As possible alternative options for restoring the required level and salinity of the Kuialnyk Liman water, the option of supplying water from the Dniester River, located at a distance of 40-50 km, and drinking water from the 'Infox' LLC ('Infoxvodokanal') was considered [34]. However, after a comprehensive review, it was concluded that the replenishment of the Kuialnyk Liman with drinking water in modern conditions is not economically feasible, due to its high cost.

Thus, this object is potentially suitable for placing SGP plant operating on the principle of mixing sea water and a hypersaline solution of the Kuialnyk Liman waters.

3. *Sasyk-Sivash Lake* is located in the western

part of the Crimea and belongs to the Yevpatoria group of salt lakes, formed from shallow sea bays and lagoons of the Kalamitsky Bay, separated from it by narrow sandbars [35]. The lake area is approximately 75.3 km^2. The drainage area is about 1064 km^2. In 1962, in order to increase the salt concentration and optimize the receipt of raw materials for a chemical plant, from Cape Krasny, located on the eastern shore of the lake to the outskirts of Yevpatoria, a dam about 9 km long was built, dividing Sasyk-Sivash Lake into the northern one, subject to freshwater runoff, and the southern part. After the construction of the dam, two completely different reservoirs were formed. The northern part is connected to the Karaymskyi Liman, which, in turn, is connected to the Kalamitsky Bay of the Black Sea. According to the data [36], water salinity in the northern part ranges from 6.6 to 11.1 ‰ and depends mainly on the wind regime and waves. The southern part is drainless hypersalty with salinity up to 316.1 ‰. In areas located at some distance from the dam in the southern part of the lake and directly at the dam, salinity is lower and on the surface is 184.4-272.8 ‰. Sasyk-Sivash Lake, as well as the Kuialnyk Liman, in the future can be considered as a potential object for the placement of an SGP power plant operating on the principle of mixing sea water and hypersaline solution.

4. *Sivash* is a vast shallow bay of the Azov Sea, with a rugged coastline, many peninsulas, capes, bays. Sivash is connected to the Azov Sea by the shallow and narrow Genichesk Strait, located at the northern end of the Arabat Spit. The Chongar Peninsula divides the Sivash into two parts: western and eastern [37]. The total area of Sivash is about 2530-2540 km^2 (1430 km^2 – the eastern part, 1100 km^2 – the western part, which is the largest of the considered reservoirs). Under natural conditions, the area of the eastern part of Sivash changes little during the year, while the western part, depending on meteorological and hydrological conditions, sharply doubles in winter and is largely dried up in summer, turning into extensive salt droughts.

Currently, two artificial dams, with the help of which the hydrochemical regime and the supply of brine are regulated, divide the Sivash into three separate parts: Eastern, Central and Western Sivash (Fig. 4).

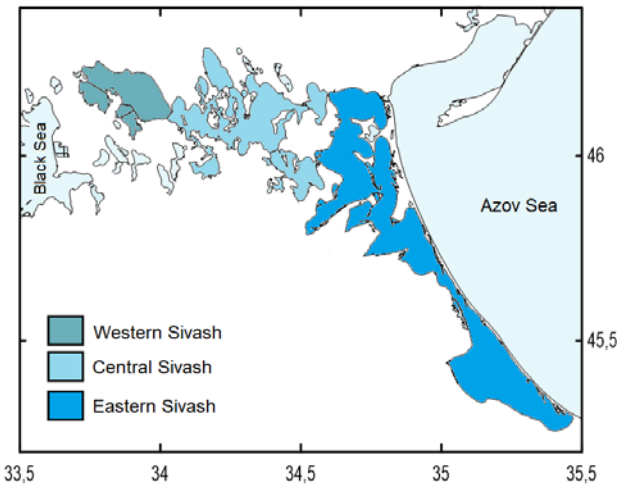

Fig. 4. Map of Sivash

In general, Sivash is very shallow, it is characterized by depths < 0.5 m (32 % of its area), and less than half (46 % of its area) falls at depths of 1.0-2.5 m. Before the construction of the dams, the brine concentration in the western part of the Sivash experienced significant changes (from 50.0 to 260.0 ‰). After the construction of the dams, the western part was turned into an isolated basin with controlled hydrological and hydrochemical regimes, and the selected Middle reservoir was turned into a huge evaporation basin for the preparation of high-concentration brines. The brine of the Western Sivash enters through the brine pipeline to the Aigul Lake, which has been turned into an intermediate brine storage, and then to the Old Lake, from where the brines are fed to the plant for processing (plants were built on the basis of Sivash: Perekop Bromine Plant, Crimean Titanium Dioxide Plant for the manufacture of phosphate fertilizers and Crimean soda plant were built [38]. The Western Sivash is used to obtain concentrated brine for the production of magnesia products, gypsum and bromine, as well as a large amount of sodium chloride. The value of overland flow, reaching 7.2 million m^3 in a dry year, 24.3 million m^3 on average, and 60.5 million m^3 in a rainy year, is commensurate with the evaporation of brines in the Western Sivash, which is equal to 25.6 million m^3 per year under steady hydrological and hydrochemical regimes.

The salinity of the brine in different parts of the Sivash is not the same and changes over time and depends on the totality of the life conditions of the reservoir – currents, meteorological and hydrological factors. The waters of the Azov Sea with a salinity of

11.0-12.0 ‰ enter to the Eastern Sivash [39]. When the waters move to the west, the concentration of brine occurs and at *Cape Kugaran* it already reaches 230.0-260.0 ‰. On average, salinity in the eastern part of the Sivash ranges from 115.0-135.0 ‰. In the western part, after the construction of dams, salinity is maintained at the level of 240.0-260.0 ‰. The brines of the Eastern Sivash are distinguished by the greatest constancy of salinity, where seasonal fluctuations do not exceed 15.0-20.0 ‰. The period of maximum brine concentrations lasts from June to October-November, when evaporation is approximately three times higher than overland flow and precipitation. In the Western Sivash, before regulation, sharp fluctuations in salinity were typical. As a result of surge currents and overland flow, the concentration of brine decreased over several days from 260.0-270.0 ‰ to 50.0-70.0 ‰.

Thus, the Western Sivash with its large reserves of highly concentrated brine is a good source of hypersaline solution for the SGP power plant. The source of water with low salinity in this case can be the waters of the Karkinitsky Bay of the Black Sea (salinity 15.0-18.0 ‰ [40]), remote from the western tip of the Western Sivash at a distance of 9.5 km near Armiansk. Moreover, today there is a channel connecting the Karkinitsky Bay and the Western Sivash, which reduces the cost of building infrastructure associated with the SGP power plant.

The results of calculating the maximum net power for the above objects are shown in Table 2, where c_D – average concentration of brine in limans, c_F – salinity in the area of the proposed water intake in the Black Sea (the Danube River in the case of the Alibey and Shagany limans).

Table 2

The maximum net power W_{net}^{max} (МВт) per 1 m^3 of solution passing through the membrane

Object name	**Area, km^2**	**Summer**			**Winter**		
		c_D, ‰	**c_F, ‰**	**W_{net}^{max}, MW/m^3**	**c_D, ‰**	**c_F, ‰**	**W_{net}^{max}, MW/m^3**
Alibey	98	48-54	0	1.91-2.15	25	0	0.9
Shagany	71	45-53	0	1.79-2.11	25	0	0.9
Kuialnyk	25-60	320	14	12.2	200	14	6.67
Sasyk- Sivash	75,3	272	18	10.29	184	18	5.96
Western Sivash	1100	260	18	9.65	240	15	8.07

As can be seen from Table 2 highest values W_{net}^{max} obtained in the summer months, when the salinity in limans reaches its maximum and, consequently, its difference with the salinity of sea (river) water increases. Proceeding from W_{net}^{max}, obtained for the Western Sivash, where the salinity is maintained artificially at certain values, it can be seen that the annual amplitude has a smaller value, which provides more stable conditions.

Conclusions. There are objects in the northwestern Black Sea region, in the waters of which, as soon as technologies become available, it will be possible to implement SGP projects. The Kuialnyk Liman, Sasyk- Sivash lake and Western Sivash have the most favorable conditions, where the highest power indicators are shown when using the sea water – hypersaline solution scheme, in which freshwater is not consumed. Taking into account the shortage of freshwater resources and, based on the trend of climate change in the northwestern Black Sea region towards the development of arid conditions, the need for their conservation in this region will continue to increase. At the same time, these same changes already today lead to a change in the hydrological regime of the estuaries of the northwestern Black Sea region, as a result of which the water content is reduced and mineralization (salinity) increases. Such changes negatively affect the state of aquatic ecosystems and the conduct of traditional economic activities, which makes the economic condition of local communities unsustainable. If the technical problems associated with the implementation of SGP projects are successfully resolved, this would provide the population with additional energy, and also help to preserve the natural state of the estuaries that are in the process of degradation.

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Використання енергії градієнта солоності в причорноморських регіонах (в рамках розвитку «блакитної» технології)

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Сьогодні людство знаходиться в пошуку нових джерел енергії, щоб зробити економіку стійкішою, а також необхідністю переходу до енергетики, що працює на принципах Carbon-Free Technology. Для Чорного моря це виявляється у прагненні успішної реалізації програми Blue Growth Accelerator, націленої на впровадження інноваційних технологій та альтернативних джерел енергії в енергетику Причорноморських країн, для розвитку «Блакитної економіки» та досягнення здорового, продуктивного та сталого його стану. Взаємодія прісної та солоної води може дати, по суті, необмежену, безкоштовну та чисту енергію. В основі вироблення такої енергії лежить так званий градієнт солоності, що виникає при змішуванні двох видів води. Після десятків років роботи та численних експериментів вчені розробили спосіб використання енергії градієнта солоності для отримання електрики. Такий вид електроенергії також називають «блакитний» (англ. Blue Energy), за асоціацією з кольором змішування прісної води та солоною при впаданні річок в океан. Місця (устя або дельти), де річки впадають в океани і моря, очищені завдяки фізико-хімічним процесам, що відбуваються під час змішування прісної та солоної води, мають воістину величезний енергетичний потенціал. У північно-західному регіоні Чорного моря, вздовж узбережжя між річками Дунай і Дніпро, є 21 лиман, деякі можна використовувати для генерування градієнта солоності. Метою роботи є визначення районів з необхідними умовами для використання енергії градієнту солоності, а також оцінка їх потенціалу на прикладі оцінки максимальної теоретичної потужності системи PRO. Результати розрахунку максимальної потужності показали, що найбільші значення отримані в літні місяці, коли солоність в лиманах досягає максимуму і, отже, збільшується її різниця з солоністю морської (річкової) води. Найбільш високими показниками максимальної теоретичної потужності мають Куяльницький лиман, озеро Сасик-Сиваш та Західний Сиваш, де йдеться про використання схеми морська вода – гіперсолоний розчин, за якої не витрачається прісна вода.

Ключові слова: *енергія градієнту солоності, осмос із затримкою тиску, зворотній електродіаліз, Північно-Західне Причорномор'я, Чорне море, Блакитне зростання, відновлювана енергія.*

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