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**HYDROGEN SULFIDE ENERGY OF THE BLACK SEA****N.A. Azarenkov<sup>1,2</sup>, B.V. Borts<sup>1</sup>, V.I. Tkachenko<sup>1,2</sup>**<sup>1</sup> *National Science Center «Kharkov Institute of Physics and Technology»**1, Akademicheskaya St., Kharkov, 61108, Ukraine*<sup>2</sup> *V.N. Karazin Kharkiv National University**4, Svobody Sq., Kharkov, 61022, Ukraine**e-mail: [tkachenko@kipt.kharkov.ua](mailto:tkachenko@kipt.kharkov.ua)*

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The word combination "hydrogen sulfide energy" was implemented after a series of publications dedicated to solving the problem of obtaining the energy from hydrogen sulfide of the Black Sea. This direction of research is a part of area of expertise which recently has been intensively developing – hydrogen sulfide energy. It is known that there is no hydrogen sulfide in the Black Sea in a thin surface layer with thickness 100 - 150 m, with a maximum depth of the basin about two kilometers. Starting from the depths of 100-150 m the concentration of hydrogen sulfide is increasing and reaches the value of ~ 10 mg/l at the bottom of the sea. Extraction of the hydrogen sulfide accumulated in waters of the Black Sea is a serious problem. Therefore, at present, a big number of technologies were offered to obtain hydrogen sulfide from waters of the Black Sea. All of them are resource and energy-consuming. The most preferable one, according to the stated parameters, is the hydrogen sulfide gas-lift technology of delivering water at a certain height above the sea level, its decontamination due to fast decompression, and subsequent discharge to a depth where the concentration of hydrogen sulfide corresponds to its concentration in the discharged water. Ecological risks appear when implementing such a technology, which may be leveled by conducting of special activities. Hence, implementation of gas-lift technology provides delivery of big volumes of deep sea waters at the level higher than the sea level, there is a possibility of additional obtaining of energy due to differences in temperatures, salinity of surface and deep waters, as well as hydrostatic power of water lifted at certain level above the sea level. If such energy generating facility can be constructed on the bases of floating platform, then there is a possibility to increase the generating capacity of the complex using energy of waves, wind and the sun. Thus, this paper provides the possibility of creating a floating power generating facility for extraction of different types of energies that are concentrated in the Black Sea.

**KEYWORDS:** hydrogen sulfide energy, Black Sea, gaslift technology, waves, wind, sun, floating power generating facility

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Словосполучення "сірководень енергія" було запропоновано після серії публікацій, присвячених вирішенню проблеми отримання енергії з сірководню Чорного моря. Цей напрямок досліджень є частиною галузі знань, яка останнім часом інтенсивно розвивається - сірководнева енергетика. Відомо, що в Чорному морі в тонкому поверхневому шарі товщиною 100 - 150 м, при максимальній глибині басейну близько двох кілометрів, не міститься сірководень. Починаючи з глибини 100-150 м концентрація сірководню збільшується і досягає значення ~ 10 мг / л біля дна моря. Видобуток сірководню, накопиченого в водах Чорного моря, є серйозною проблемою. Тому до теперішнього часу було запропоновано велику кількість технологій для отримання сірководню з води Чорного моря. Всі вони ресурсо- і енергоємні. Найбільш кращим, відповідно до зазначених параметрів, є газліфтна технологія підйому морської води на певну технологічну висоту над рівнем моря, її дегазація внаслідок швидкого зниження тиску, і подальший злив на глибину, де концентрація сірководню відповідає його концентрації у воді, що зливається. Реалізація такої технології пов'язана з екологічними ризиками, які можуть бути вирішені шляхом проведення спеціальних заходів. Отже, реалізація газліфтної технології забезпечує доставку великих обсягів глибинних морських вод на рівень вище рівня моря, де виникає можливість додаткового отримання енергії за рахунок різниці температур, солоності поверхневих і глибинних морських вод, а також гідростатичної енергії води, піднятої на певну висоту над рівнем моря. Якщо такий енергогенеруючий комплекс буде побудований на основі плаваючої платформи, то виникає можливість збільшити його енергогенеруючу потужність в результаті використання енергії хвиль, вітру і сонця. Таким чином, в роботі пропонується створення плаваючого енергогенеруючого комплексу для видобування різних видів енергії, які зосереджені в Чорному морі.

**КЛЮЧОВІ СЛОВА:** енергія сірководню, Чорне море, газліфтна технологія, хвилі, вітер, сонце, плаваючий енергогенеруючий комплекс

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Словосочетание "сероводород энергия" было предложено после серии публикаций, посвященных решению проблемы получения энергии из сероводорода Черного моря. Это направление исследований является частью области знаний, которое в

последнее время интенсивно развивается- сероводородная энергетика. Известно, что в Черном море в тонком поверхностном слое толщиной 100 - 150 м, при максимальной глубине бассейна около двух километров, не содержится сероводород. Начиная с глубины 100-150 м концентрация сероводорода увеличивается и достигает значения  $\sim 10$  мг/л у дна моря. Добыча сероводорода, накопленного в водах Черного моря является серьезной проблемой. Поэтому до настоящего времени было предложено большое количество технологий для получения сероводорода из воды Черного моря. Все они ресурс- и энергоемкие. Наиболее предпочтительным, в соответствии с указанными параметрами, является газлифтная технология подъема морской воды на определенную технологическую высоту над уровнем моря, ее дегазация вследствие быстрого снижения давления, и последующий слив на глубину, где концентрация сероводорода соответствует его концентрации в сливаемой воде. Реализация такой технологии связана с экологическими рисками, которые могут быть решены путем проведения специальных мероприятий. Следовательно, реализация газлифтной технологии обеспечивает доставку больших объемов глубинных морских вод на уровень выше уровня моря, где возникает возможность дополнительного получения энергии за счет разности температур, солености поверхностных и глубинных морских вод, а также гидростатической энергии воды, поднятой на определенную высоту над уровнем моря. Если такой энергогенерирующий комплекс будет построен на основе плавающей платформы, то возникает возможность увеличить его энергогенерирующие мощности в результате использования энергии волн, ветра и солнца. Таким образом, в работе предлагается создание плавающего энергогенерирующего комплекса для извлечения различных видов энергии, которые сосредоточены в Черном море.

**КЛЮЧЕВЫЕ СЛОВА:** энергия сероводорода, Черное море, газлифтная технология, волны, ветер, солнце, плавающий энергогенерирующий комплекс

European Union (EU) has set a goal to increase the production of energy from the renewable energy sources (hereinafter. RES) up to 12% by 2010 with the approximate share of 6% in 2000. However, the corrected and a more pessimistic outlook based on the dynamics shown by the introduction of the RES introduction in the EU, shows the real value of the achievable share in the total energy balance of 8 – 10 % [1].

The share of energy production in Ukraine using RES is less than 1 % of all its fuel and energy resources [2]. The share of alternative power industry is planned to increase up to 10 % by 2010. Such prediction is based on the fact that the potential of natural resources for the development of alternative energy in Ukraine is not inferior to most countries in the European Union. This ratio is also confirmed by the study of RES potential carried out by the National Academy of Sciences which rates the possibility to use wind energy, solar energy, energy of small rivers, biomass energy, geothermal energy, the surrounding area energy, energy of the dumped energy and technological potential, unconventional fuel energy.

Necessity to develop the alternative power industry in Ukraine is also conditioned by extreme degradation of energy complex, considerable expenses on import of energy resources, availability of a well-developed industrial infrastructure for power plants, environmental issues associated with the fuel and energy complex.

Thus, the search for alternative environmentally friendly energy sources can now be attributed to the most relevant and promising for the power industry of Ukraine. According to one of the working hypotheses, actively discussed at present, hydrogen can be used to obtain such type of fuel because it is an environmentally friendly energy resource. Use of technology for hydrogen extraction from natural hydrogen sulfide of the Black Sea deep waters would be one of the possible methods to obtain hydrogen along with utilization of electricity overproduced by nuclear power plants (water electrolysis).

It should be noted that possible volumes of hydrogen sulfide energy use are not considered in the balance of RES sources in Ukraine, as well as related wave, wind, heat and related salinity gradient energies of the Black Sea region.

The following discussion will focus on the status, problems and prospects of energy utilization Black Sea hydrogen sulfide.

The aim of this work is discussion of the status, problems and prospects of energy utilization Black Sea hydrogen sulfide and other types of renewable, alternative energy sources of the Black Sea region.

## **STATUS, PROBLEMS AND PROSPECTS OF HYDROGEN SULFIDE POWER INDUSTRY OF THE BLACK SEA**

### **Hydrogen sulfide resources of the Black Sea**

Let's discuss the basic facts related to generally accepted points of view on formation, detection, reproduction and distribution of hydrogen sulfide in the Black Sea [3]. This information has a fundamental meaning. The fact is that until recently, there exists a point of view about the irrationality of extraction of hydrogen sulfide from the sea water due to unpredictable ecological consequences and low energy efficiency of the expected effect due to low concentration of hydrogen sulfide. In our article we will try to present our vision of the possibility to use hydrogen sulfide resources of the Black Sea based on up-to-date technological developments concerning its extraction and its ecologically safe disposal.

**Chronological background.** Dense Mediterranean waters reached the Bosphorus about 9 000 years ago due to global warming and sea level rise, and that was the start of their entry into the freshwater Black Sea Basin. This led to a stable salinity of lower layers of water, displacement and rise of deep and new-euxine waters, rich in nutrients, into euphotic area; significant increase of biological capacity of the basin which was followed by concentration of organic matter in water and sediments. Simultaneous development of density stratification limited sharply the flow of oxygen into

deep waters where it was consumed intensively by oxidation of a large number of deposited organic matters. As a result of these processes, a constant area with anaerobic conditions was formed 7 000 – 8 000 years ago in deep sea layers and later it reached a modern physical and chemical state after a number of transformations.

**Sources of hydrogen sulfide flow into the Black Sea waters.** First, existence of deep waters infection was found by N.I. Andrusov, the Assistance Professor of the Novorossiysk University, during participation in an oceanographic expedition to the Black Sea in 1890. According to his proposed theory, hydrogen sulfide was extracted during the decomposition of organisms that became extinct not long ago.

In 1891 N.D. Zelinskiy, Assistant Professor, had another opinion on occurrence of hydrogen sulfide in the Black Sea waters. Based on analysis of soil samples from different depths in different areas of the Black Sea he convincingly demonstrated that hydrogen sulfide in seawater is a waste product of special bacteria that live in the bottom of the sea.

Analysis of literature data available at present allows to make a conclusion that there are three basic sources of H<sub>2</sub>S flow into water reservoirs of the Earth and they are different by significance. Relatively they could be divided by the method of hydrogen sulfide flow into water.

The first source provides its flow as a result of renewal of sulfides that are in the water and occur during decomposition of organic matter.

The second source supplies hydrogen sulfide that occurs during the decay of organic matters.

The third source delivers hydrogen sulfide from cracks of the earth crust, i.e., has a volcanic origin (hydrogen sulfide of hydrothermal waters or oil layers).

According to many researchers opinion, the considerable part of the Black Sea hydrogen sulfide is obtained in surface layer of sediments of anaerobic area. Yu. I. Sorokin in 1960 investigated for the first time the intensity of sulfide reduction in deep Black Sea sediments. He found that the most intensive process of hydrogen sulfide formation occurs in the surface layer of the bottom sediments with thickness of 1-2 cm. The rate of sulfide reduction decreased in 20-30 times on the depth of 5 cm in comparison to surface, and this process was not observed at all on the depth of 10 cm.

Intensity distribution of sulfide reduction along the area of the sea floor is not uniform. The maximal values are recorded on slopes in periphery regions (50-100 mg/m<sup>2</sup> per day), minimal – cholestasia area (1-5 mg/m<sup>2</sup> per day).

Based on available data we calculated the annual production of sulfur renewed from hydrogen sulfide area of sediments (5,53 x 10<sup>6</sup> t/year) and quantity of the renewed sulfur accumulated in sediments (0,28 x 10<sup>6</sup> tones). The total H<sub>2</sub>S sulfur flow into water is calculated as difference between total produced and accumulated sulfur – 5,25 x 10<sup>6</sup> t/year. In terms of H<sub>2</sub>S it is 5,58 10<sup>6</sup> t/year.

Presence of sulfide reduction process in sediments is undoubtful, but the direction and volume of hydrogen sulfide flow over the water-sediment boundary could be judged only by knowing laws of its distribution in silt and bottom waters.

Comparison of data on hydrogen sulfide distribution in bottom and silt waters of surface sediments demonstrate that entry of H<sub>2</sub>S from sediments into water could occur only in areas of slope and periphery of a cavity. H<sub>2</sub>S concentration in silt waters is essentially less than in the sea bottom along the huge areas of deep sea waters, and its diffusion from sediments is impossible. Thus, experimental data do not confirm the widespread idea that the sea bottom sediments along the entire area of anaerobic zone are the source of hydrogen sulfide in the water depths of the basin.

Generally, the sea bottom sediments not only consume hydrogen sulfide from water in approximate quantity of 4x10<sup>6</sup> t/year but also generate about the same quantity of hydrogen sulfide (3-5)x10<sup>6</sup> t/year.

Formation of hydrogen sulfide due to sulfide reduction in the Black Sea occurs not only in sediments but in the water depths as well. The most actively this process occurs under the upper boundary of hydrogen sulfide distribution in the layer of maximum intensity of its oxidation. 48,5-111,5 (average is 80) mg of H<sub>2</sub>S (m<sup>2</sup>/day) are formed in depths of 180-300 m with 9°C or 8,7 x10<sup>6</sup> t of H<sub>2</sub>S/year, and 1,35-64,5 (average is 33) mg of H<sub>2</sub>S/ (m<sup>2</sup>/day) or 3,6x10<sup>6</sup> t of H<sub>2</sub>S/year are formed in depths of 1700-2000 m.

Total production of hydrogen sulfide due to sulfide reduction in water depths of the Black Sea sediments is in 10-100 times higher than in water. It is caused by a considerable thickness of water layer (in 100-1000 times thicker than sedimentary) where sulfide reduction is observed.

Huge influence of water layer thickness on total production of hydrogen sulfide is evident in consistent pattern of H<sub>2</sub>S distribution in the Black Sea. On the horizons of 800-1500 m the concentration of hydrogen sulfide in water above the slope and on the periphery of deep-water cavity is higher than in central areas of sea. It is because the intensity of sulfide reduction in water above the slope is higher than in central areas due to bigger quantity of fresh organic matter which is formed and flows here. Besides, the hydrogen sulfide reaches water from sediments in the slope area.

Increase of hydrogen sulfide in the Black Sea waters due to processes of sulfide reduction in water depths is dominating and is estimated as 87-96% from its total increase.

Together with the described above biogenic concepts of formation and occurrence of hydrogen sulfide in the Black Sea, there is an abiogenic (geological) concept as well. According to the latter, about 4-20 % of hydrogen sulfide come to the Black Sea in a ready form mainly from the bottom breed on tectonic faults with ground waters (for example, hydrogen sulfide sources on Eastern coast of the Black Sea in limestone of Jurassic period, resort area Matsesta) and from oil layers.

The date given above allows to consider the Black Sea as one of the world hugest hydrogen sulfide deposit which,

in fact, could be a source of commodity sulfur as well as energy. If to assume that annual increase of hydrogen sulfide of the Black Sea is not less than 4-9 million of tones, then the total of its reserves could be estimated by fairly impressive value of 28-63 billion of tones. Rational and ecologically friendly use of at least the reproductive part of H<sub>2</sub>S could give an essential supplement to energy balance of Ukraine and, which is more significant; it could stop the further increase of hydrogen sulfide contamination. Supplies of hydrogen sulfide in the Black Sea are renewable in contrast to other fossil minerals, which is very important as well.

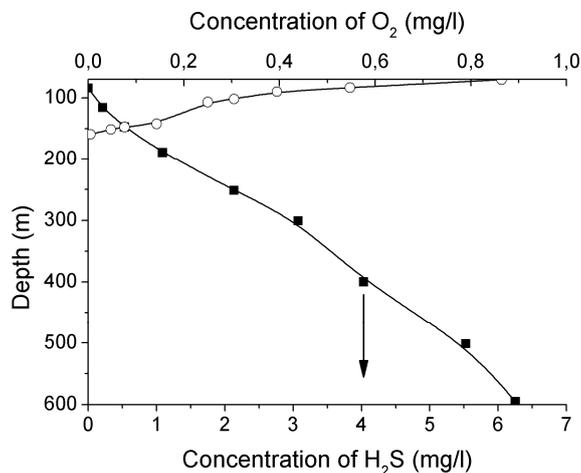


Fig. 1. Average vertical distribution of O<sub>2</sub>, H<sub>2</sub>S [3] along the defined sea are.

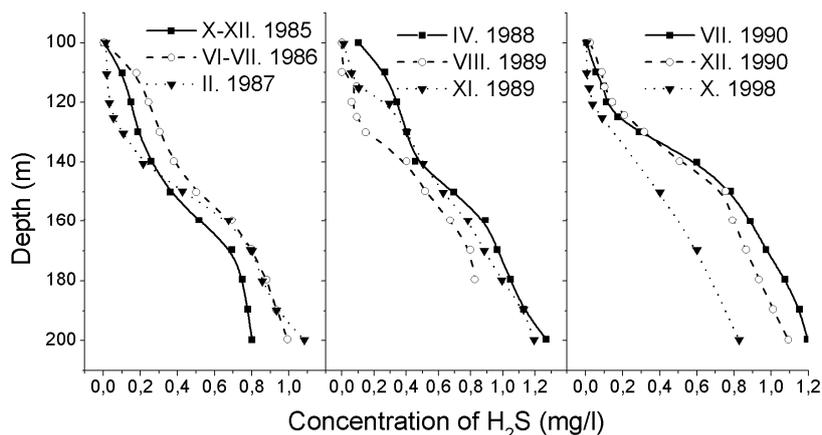


Fig. 2. Average vertical distribution of H<sub>2</sub>S in mg/l along the defined sea area [3].

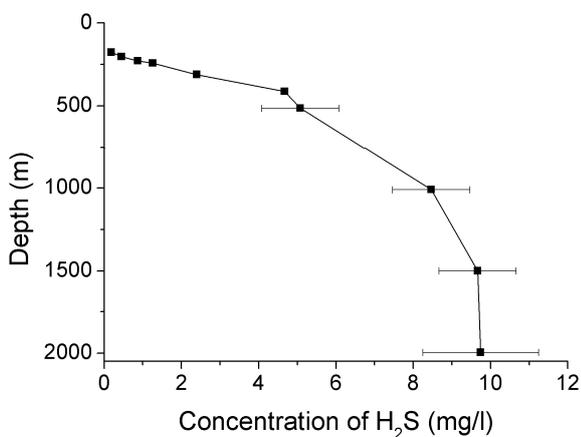


Fig. 3. Concentration of H<sub>2</sub>S (mg/l) in the Black Sea [3].

Hydrogen sulfide concentration on the surface waters is controlled by its oxidation. Fig. 1-3 shows the average oxygen (O<sub>2</sub>) distribution along the defined sea area, and from data given in the figures it is clear that the average quantity of H<sub>2</sub>S dissolved in the Black Sea, based on one liter of sea water is: 1.2 mg – at a depth of 200 m, 2.34 mg – at a depth of 300 m, 8.84 mg – at a depth of 1000 m and 9.6 mg – at a depth of 2000 m.

It should be noted that the levels of hydrogen sulfide in seawater given above are in 1000 times smaller from saturation concentration (hydrogen sulfide solubility at standard conditions is 4.62 ml per 1 ml of water which is equal to 7 g per 1 liter of water).

Atmospheric oxygen, which dissolves in water, reacts with hydrogen sulfide, turning it into sulfuric acid. Acid reacts with mineral salts dissolved in water thus forming sulfates. These processes occur simultaneously, making the Black sea a dynamic equilibrium and maintaining almost constant depth near-surface area free from hydrogen sulfide. Calculations show that not more than one quarter of hydrogen sulfide is converted into sulfates per year as a result of oxidation in the Black Sea.

If annually remove from the Black sea about 25 million tons of hydrogen sulfide it would be equal to obtaining

energy of about 9.25 billion kilowatt-hours (burning of one kilogram of hydrogen sulfide gives energy of 1334 kJ, and kilogram of methane – 2044 kJ). This rate is 6.3 % of the RF NPP power production (147.6 billion of kilowatt-hours in 2005) and 10.4% of Ukrainian NPP power production (88.782 billion of kilowatt-hours in 2005).

Thus, the Black Sea as the source of hydrogen sulfide could provide an essential supplement into the energy balance of Ukraine. But how to implement this idea in practice?

### Methods of hydrogen sulfide extraction

The solution of technical task of H<sub>2</sub>S extraction from seawater is caused by the following factors which are different on complexity:

- H<sub>2</sub>S is present in seawater in both free and bound states as a part of hydrosulfates. Taking into account the above mentioned data, one tone of deep water contains from 1.2 up to 10 g of H<sub>2</sub>S and its compounds;
- the problem of raising the saturated deep sulfurous mass of sea water;
- the allocation of hydrogen sulfide extraction from sea water.

Existing proposals and methods in this area have varying degrees of testing and, as a consequence, their real options for technical implementation.

Let us consider some of them.

Available proposals and practices in this area have different degree of testing and, as a result, options of their technical implementation. Consider some of them.

The [3] describes the proposal of raising the bottom layers of seawater from areas with abnormally high levels of hydrogen sulfide composition on certain technological height, where it is then exposed to electro hydraulic impact which provides the separation of hydrogen sulfide, and return the treated water back into the Black Sea.

Other project offers to use the membrane absorbers with high-selective modified membrane (for example, sulfur gel, sulfacil) or glycol and amines straight at depth. H<sub>2</sub>S is dissolved in these absorbers hundreds of times better than in seawaters which makes very efficient extraction of H<sub>2</sub>S from seawaters with its further extraction on the surface.

The same project offers a method to extract the hydrogen sulfide from seawater based on the fact that under the effect of ultraviolet radiation of a specific wavelength (180-253 nm) H<sub>2</sub>S selectively dissociates into hydrogen and sulfur  $H_2S + h\nu \rightarrow H + HS$ . During implementation of this method it is offered to place the powerful source of UV radiation at a required depth where photo dissociation of H<sub>2</sub>S and hydrosulphites will occur. The resulting hydrogen will rise along with the water-insoluble sulfur.

Promising is to use ozone, bubbled into the seawater to the required depth for oxidation of hydrogen sulfide and hydrosulphites. The method is based on the known technology for purification of reservoir and drainage waters of sulfur plants. The sense of this method is in oxidation of hydrogen sulfide in water by ozonated air to form water and sulfur.

A rather elegant solution is offered to treat the seawater by UV or ozone without lifting it to the surface: to put down to a depth a pipe with the closed bottom part and specially shaped holes from which water jets ( $V \sim 100$  m/s) are scattered at the bottom level of pipe and vibrator under influence of hydrostatic pressure. H<sub>2</sub>S and hydrosulphites extraction and dissociation occurs in the tube due to such physical influences. The formed gas is pumped out to the surface, the aerosols are condensed on walls, flow down into special modules from which a condensate is pumped to the surface or into the sea.

Appealing is the copyright certificate for the method to clean natural reservoirs from hydrogen sulfide where it is offered to use vertical channel with rigid walls in the sea. Raising the water by this pump from this channel once, one can get gas and water fountain due to difference in the sea hydrostatic pressure at the level of lower-cut of the channel and mixture of gas and water pressure at the same level inside the channel. Thus, according to the authors, there is almost no need to spend energy on pumping the deep layers to the surface to lift the hydrogen sulfide masses from the sea bottom using the so-called air-lift effect (gas lift). The essence of this is the following.

Vertical plates, for example, from activated aluminum which is typically used in the galvanic protection of ship hulls, are placed in the bottom part of the tube (channel) to provide the upward water movement along the tube. In interaction with seawater such an alloy partially decomposes water, emitting the hydrogen. Hydrogen, going upwards, takes water with it along the tube (primary air-lift). The dissolved hydrogen sulfide starts its emission from water-hydrogen mixture that moves to the water surface due to pressure drop and, thus, enhancing the air-lift effect.

We propose a method to extract hydrogen sulfide from natural aquatic environment and from deep water layers of the sea by acidizing the sour water with a mineral acid and its aerating. According to the authors of the project, part of the sulfuric acid obtain here with is assumed to use for acidizing the initial water, and to dispose the heat obtained as a result of hydrogen sulfide oxidation.

### Methods of disposal (dissociation) of hydrogen sulfide

In addition to the problem of hydrogen sulfide disposal from natural ponds there is also a problem of disposal of hydrogen sulfide obtained as a result of different multi tonnage technological experiments. Thus, for example, in a concentrated form it is formed during hydro treatment of oil, during extraction from natural, technological and ventilation gases. Studies in this area are directly related to the problem of disposal of hydrogen sulfide from the Black Sea.

A method to produce electricity from the Black Sea water by extracting hydrogen sulfide from it and its burning in

gas-turbine machine, is given in [3] and it was developed by other authors. Here, characteristics and scheme of power plant with 10 MW power are given and estimation of economic efficiency as well. However, direct burning of hydrogen sulfide is not the only one method to obtain energy. Besides, this method has an essential disadvantage: associated gases are emitted into the environment and require use of highly expensive purification.

One of the possible methods to eliminate this disadvantage is to use such methods of hydrogen sulfide dissociation as plasma-chemical, radiation (radiolysis), thermal and photolysis.

Works in the area of plasma-chemical dissociation have been carried out for a long time already and they are successful. These studies offer a cost-effective diagram of the technological process of plasma-chemical dissociation of hydrogen sulfide to produce two valuable products – polymeric sulfur and hydrogen.

One of the methods to obtain hydrogen both from water and hydrogen sulfide is radiolysis.

Values of radiation yield of hydrogen  $G(H_2)$  for pure water are in the range from 0.45 up to 1.65 mol./100 eV depending on conditions and radiation. It is possible to increase significantly  $G(H_2)$  at radiolysis of powder-like hydroxides or hydrates that restore by water or steam during dehydration. In this case, radiation yield of hydrogen is in average of 20.41 mol./100 eV.

Studies of radioactive decomposition of hydrogen sulfide are of specific interest for obtaining hydrogen from hydrogen sulfide. Experiments in this area were performed in two stages.

The first stage includes series of experiments performed on pure hydrogen sulfide (temperature - 250 °C, radiation dose – 1.5 Mrad).

The second stage includes decomposition of hydrogen sulfide with fine-dispersed catalyst  $Al_2O_3$  (with temperatures 200 °C and 25 °C, radiation dose  $\gamma$ -radiation was 0.5 Mrad). Results of studies are given in the Fig. 4.

As it is clear from the Fig. 4., all dependencies of gaseous hydrogen yield from density of hydrogen sulfide in the studied area have a linear character. Increasing the density of  $H_2S$  and temperature we increase the hydrogen yield.

In order to increase the hydrogen yield we experimentally exposed to ionizing radiation mixture of hydrogen sulfide with carbon monoxide. It was found, that the most optimal temperature range for this process is 400-500 °C, and radiation dose is  $(2.5-3.0) \cdot 10^{17}$  eV/cm<sup>3</sup>. Herewith, the conversion level was 50%.

With thermal dissociation of hydrogen sulfide it was shown that  $H_2S$  dissociation becomes evident starting with 400 °C and goes almost until the end with temperature of 1690 °C.

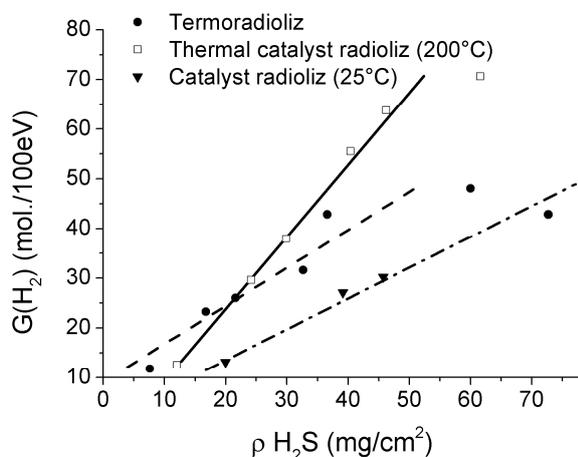


Fig. 4. Dependency of gaseous hydrogen yield from density of hydrogen sulfide  $\rho$ .

from ecological point of view, since it is related to emissions of harmful associated gases into the atmosphere. Using solar oven from ~ 3 mol of  $H_2S$  we obtain 1 mol of  $H_2$ . Therefore, the conversion level is approximately equal to 34%.

The basic principle of photolysis dissociation is to select such a wave length of luminous radiation which is subject to dissociation of the substance that this irradiation should mould meet (or should be close to maximum (pick)) of luminous absorption. Such maximum corresponds to fluctuation frequencies of atoms in molecules of this substance. These fluctuations are enhanced under light influence with the wave frequency close to the frequency fluctuation wave, since are in resonance with luminous wave similar to the dissociation process of triatomic molecule of nitrogen dioxide described in [4]. Such resonance interaction explains strong luminous absorption with the corresponding wave frequency which, as a result, leads to breaking the bonds between atoms of hydrogen sulfide.

$H_2S$  molecule has a structure close to isosceles triangle with S atom on the top of it. Angle between bonds of S with H atoms is equal to 92°13', interatomic spacing 2(S-H) is 1.336 Å. Fluctuation wavelength of hydrogen atoms with respect to sulfur atom is about 2730 Å (rather 2721.92 Å and 2733.36 Å). These frequencies are in the wavelength range of the emission spectrum of a mercury lamp (2483-5770 Å), the most intense line in this spectrum has a

Thermal dissociation of  $H_2S$  is observed also using solar oven that provides temperature of 1027-1727 °C.

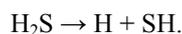
Typically, the Claus process is used to split  $H_2S$  into hydrogen and sulfur: method of industrious production of sulfur from hydrogen sulfide. However, this process is used to extract sulfur in a number of catalyst converters with Al layers with temperature of 204-260 °C, which is obtained by burning part of  $H_2S$  in the air (about 1/3).

Thus, we obtain steam as well. Associated gases are emitted into environment or undergo costly purification.

Comparison of economic and energy efficiency of the Claus process and the use of solar oven show the advantage of the later. Using solar oven instead of steam we obtain hydrogen. Heat from its burning in the air – 286 kJ/mol, and for its obtaining we spend only 124.5 kJ/mol and additional 34 kJ/mol of electric heating to heat  $H_2S$  if there is no sunshine. Besides this energy efficiency, heat on solar oven is also profitable

wavelength of  $\lambda = 2537 \text{ \AA}$  close to the oscillation frequency of the hydrogen atoms in the molecule of  $\text{H}_2\text{S}$ .

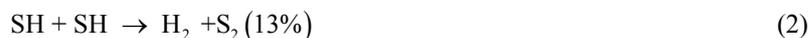
Primary action of photolysis effect on  $\text{H}_2\text{S}$  is in splitting of atomic hydrogen to form free radical SH.



Further, SH radicals and H atoms react with each other to form molecular hydrogen and sulfur. It is shown that among all possible reactions, reactions related to change in ratio between SH radicals are mainly implemented:



and



i.e., only 13% of radicals form hydrogen, and 87% of radicals react with regeneration of  $\text{H}_2\text{S}$  molecules and sulfur formation.

In order to study hydrogen one can use photocatalyst decomposition of  $\text{H}_2\text{S}$  on cadmium sulphide deposited on cation-exchange film. In some experiments films were activated by small-grain associates (new phase formation) deposited on them, containing atoms of noble metals. Thus, film with thickness of 0.3 mm of cation-exchange polymer based on sulfonated fluoropolymer MΦ-4CK similar to nafion were used. The photocatalyst film was put into the solution of  $\text{Na}_2\text{S}$  and it was irradiated with filtered light from a mercury lamp ДПИИ-1000. Results of such studies are given in the Table 1.

Table 1.

Photocatalyst activity of sulfides of Zn, Cd, Sn on polymer MΦ-4CK in reaction  $\text{H}_2\text{S} \rightarrow \text{H}_2 + \text{S}$   
 ( $\text{Na}_2\text{S} = 10^{-2} \text{ mol/l}$ ,  $\text{pH} = 10$ )

Active component of photocatalyst	CdS		CdS-Pd		CdS-Pt	CdS-ZnS	ZnS	SnS <sub>2</sub>
$\lambda$ , (nm)	436	365	436	365	436	365	436	365
Quantum yield (%)	0.00	0.08	1.5	1.5	3.0	9.5*	0.009	0.3

\*)  $\text{Na}_2\text{S} = 10^{-1} \text{ mol/l}$

As it is clear from the table, quantum yield of hydrogen increases when photocatalysts are activated by salts of noble metals.

Marginal efficiency of solar energy conversion in reaction of  $\text{H}_2\text{S}$  photocatalytic decomposition is in the range of  $\lambda > 2000 \text{ nm}$  and does not exceed 10 %. At the same time, for reaction of  $\text{H}_2\text{S}$  photocatalytic decomposition it would be reasonable to consider "commercial" marginal efficiency determined as combustion heat of the obtained hydrogen ( $\Delta H^0$ ) ratio to solar energy falling into the photocatalytic system.

For  $\lambda_{\text{nor}}=1000 \text{ nm}$  marginal efficiency is 43%, i.e., rather high. Thus, the conversion efficiency of solar energy falling on  $1 \text{ m}^2$  area on a clear day at the latitude of Novosibirsk ( $\approx 500 \text{ W/m}^2$ ) would allow to receive up to 60 l of hydrogen per hour.

Considering the above given methods of extraction and decomposition (dissociation) of hydrogen sulfide it is necessary to mention the following disadvantages:

The described methods are rather complicated and resource and energy intensive;

The descriptions almost do not contain data on economic efficiency and estimation of their use in the closed complex of energy production.

However, despite this and with appropriate improvement, separate elements of each method mentioned above could be used to create hydrogen sulfide energy generating complex (HSEGC).

Based on the given above data one can make a conclusion that it is necessary to develop the concept of optimal HSEGC.

## ENERGY FREE METHODS TO EXTRACT HYDROGEN SULFIDE WATER WITH A GIVEN WATER DEPTH

### Concept of optimal HSEGC

The problem of energy free extraction of hydrogen sulfide water of the Black Sea from the given depths is the main problem in the list of important problems (without which it is impossible to develop the concept of hydrogen sulfide power industry and creation of HSEGC on its basis). It is a key problem not only for extraction of hydrogen sulfide to the sea surface, but it has huge importance for improvement of environment ecology. Thus, in the later case it is necessary to consider the effect of positive effect of hydrogen sulfide extraction on deep sea layers (decrease of hydrogen sulfide composition on the given sea depth) and to remember that waste-water has a residual contamination by hydrogen sulfide and should be delivered to the depth which corresponds to natural level of its composition bin the sea water.

Why do authors put a question on searching for the method to extract the hydrogen sulfide water to a height of technology, and do not discuss the problem of producing the hydrogen sulfide at depth and its delivery to the sea surface?

The answer is the following:

First of all, obtaining of hydrogen sulfide at depth assumes arrangement of complicated and costly equipment on big depths in aggressive environment.

Secondly, this equipment should be either constantly moved due to the depletion of hydrogen sulfide in the surrounding layers of the water or rest still, but it would be necessary to move the water flows at big depths which is energetically unprofitable and, therefore, unrealistic.

Method to lift the hydrogen sulfide water to the level exceeding the sea level (technological height of lift) with further extraction of hydrogen sulfide by natural or some other method is an alternative to the method of hydrogen sulfide generation at depth. At the same time, the hydrogen sulfide water delivered to the sea surface will emit the hydrogen sulfide dissolved in it as a result of decrease of pressure in hundred times [5-7]. The volume of hydrogen sulfide, similar to data on preliminary oil stabilization (degassing), could reach up to 50 – 60% of its primary composition under normal conditions.

With such method we have solution to several problems that allow increasing efficiency of HSEGC work:

- Almost complete extraction of hydrogen sulfide from water and its further utilization with generation of hydrogen and polymeric sulfur;
- Generation of electric power on hydro power generators that convert into electricity the potential sea water energy lifted to technological height;
- Generation of electric power in thermal machines (for instance, Sterling engine) from the use of the temperature difference between surface and deep waters;
- Increase in received power from hydro power generators by increasing the height of the technological rise of water, caused by the use of the difference between the depth and the surface salinity of sea water.

Thus, search and justification of methods for energy profitable lift of hydrogen sulfide to a necessary technological height above the sea level is relevant and timely challenge problem to encourage the development of a fundamentally new type of hydrogen energy – hydrogen sulfide.

The task of search for energetically low cost methods to extract hydrogen sulfide water from the bottom of the Black Sea is not new. A big number of studies have been performed in this area and encouraging results have been received. However, all above described methods have either costs for electric energy or chemical reagents to ensure the lift of sea hydrogen sulfide water. Therefore, the task to search the alternative and energetically profitable schemes based on new physical mechanisms is still relevant.

The following description will focus on energetically profitable method to extract hydrogen sulfide water from the set depth of the Black Sea.

#### **Justification of possibility to lift hydrogen sulfide from the Black Sea water depths specified by gas lift**

The method to calculate the fountain oil lift in well is used to calculate the lift of hydrogen sulfide water from the bottom of the Black Sea. The fountain well operation is one of the basic methods of oil extraction. The fountain method of oil extraction is the cheapest one because it does not require additional energy costs on oil lift and only the reservoir energy is used when this method is applied.

Calculation of fountain lift comes to determination of length and diameter of eduction tube, its capacity and the pressure distribution along the depth.

Let's consider the element of the lift with length of  $dl$ . The pressure drop on this site we mark as  $dp$ . Considering the process to be static and neglecting the inertial resistance which is small in real terms, and write the equation of momentum conservation in the form of:

$$dp = \gamma_m dl + aQdl. \quad (3)$$

Here,  $\gamma_m$  – specific weight of hydrogen sulfide water which is depth function  $H$ ,  $a$  – factor that characterizes friction losses. In equation (3) we do not take into account water temperature and its effect on gas emission along the lift length.

Neglecting gas density in comparison to seawater density write the expression for gas specific weight of water-gas mixture in the form of:

$$\gamma_m = \gamma_v / (1+W), \quad (4)$$

where  $W$  – volume in relation to single water volume which is occupied by hydrogen sulfide in this section;  $\gamma_v$  – specific weight of seawater. We assume that gas solubility in seawater is described by linear law – Henry isotherm. In this case, the gas volume  $G$  emitted from one unit of seawater at pressure  $p$ , will be equal to:

$$G = G_s - \alpha \cdot (p_s - p), \quad (5)$$

where  $G$  – initial gas factor (gas saturation), i.e. the volume of hydrogen sulfide dissolved in a unit volume of liquid at saturation pressure  $p$ ;  $\alpha$  – solubility factor of hydrogen sulfide in seawater (solubility factor of gas in liquid at a given temperature, equal to the volume of the dissolved gas (in ml) per 100 g of water at a partial pressure equal to the atmospheric pressure). Please bare in mind that gas volumes  $G$  and  $G_s$  are reduced to normal conditions. Assuming gas to be ideal, from (5) we obtain that volume of the emitted gas at this depth  $G_l$  and reduced to pressure at the same depth  $p$ , is equal to:

$$G_l = \frac{G \cdot p_0}{p} = \frac{G_s - \alpha(p_s - p_0)}{p} p_0. \quad (6)$$

If gas bypass is small, i.e., relative velocity of gas bubbles and seawater is small in comparison to speed of lift, then we can put  $W = G_l$ .

Similar to gas-oil lifts, we will assume that partial phase separation and formation of “gas bearing” near pipe walls is observed for the lift of hydrogen sulfide water as it moves in the trunk blower. The reason for such phenomenon is the following. Presence of parabolic velocity profile of the liquid (Poiseuille profile), leads to different velocity of gas bubble regarding the liquid at its different points (bubbles) of the surface. Since the gas bubble moves somewhat faster than liquid, then, the liquid velocity regarding the bubble surface from the side turned to the pipe wall is bigger than from the side which is closer to the pipe centre. Thus, in cross-section of the pipe there is a pressure drop directed from the axes of the pipe to the wall. Under the effect of this pressure drop there is a displacement of bubbles to the periphery (wing lift effect). As a result, gas bubbles are concentrated near the pipe surface, the near wall gas layer occurs and it decreases dramatically the loss of gas-water mixture for friction.

Minor value of friction forces is confirmed by calculations and practical results of lifting of gas-oil mixtures. In the calculation of trunk blowers for gas-oil mixtures the practice shows that friction losses in trunk pipes are typically minor and do not exceed several percents from total pressure drop along the lift length between bottom hole and entrance. The lift, where the phase slip and losses are neglected, is called “ideal”. Thus, in further calculations we will neglect the latter component in the right part of the equation (3).

For equilibrium conditions with fixed temperature according to Gibbs phase rule (J. W. Gibbs found that the number of coexisting equilibrium in any system of phases cannot be greater than the number of generators of these components plus phase, usually, 2 (published in 1876)) the status of the system is determined by a single parameter – pressure and for non-equilibrium conditions – another parameter is velocity of pressure change in the system  $dp/d\tau$ .

One can consider the hydrogen sulfide water lift process under nonequilibrium conditions. Let the equilibrium solubility isotherm is described by a linear Henry law:  $G = \alpha \cdot p$ , and the nonequilibrium process of gas emission (hydrogen sulfide) – by equation [5]:

$$t_0 \frac{dG}{dt} + G = \alpha \cdot p, \quad (7)$$

where  $t_0$  – relaxation time.

Since the defining parameters in equation (7) are pressure  $p$  and its time derivative  $dp/d\tau$ , it is not difficult to obtain its solution in general form:

$$G = \alpha \cdot \left[ p - \int_0^t \exp\left(-\frac{t-\tau}{t_0}\right) \frac{dp}{d\tau} d\tau \right]. \quad (8)$$

Solution (8) can be analyzed. Equation (8) corresponds to the Henry law at very small pressure rates in the system ( $dp/d\tau=0$ ), as well as at very small relaxation time, i.e., at instant relaxation time ( $t_0 \rightarrow 0$ ). At finite values of  $dp/d\tau$  the dissolution curve is characterized by hysteretic dependence: when pressure is reduced  $dp/d\tau < 0$  then nonequilibrium curve is above the equilibrium  $G = \alpha p$ , i.e., gas emission is reduced as compared with equilibrium process and at  $dp/d\tau > 0$  – below the equilibrium curve the gas emission increases compared to equilibrium process.

This concept can be used to calculate fountain lift. Operation of perfect lift for gas-water mixture can be considered to determine its basic qualitative and quantitative characteristics.

Under equilibrium conditions the pressure dependence in fountain lift from the depth is determined by equation, that follows from (3) and (5):

$$\frac{1}{\gamma_v} \frac{dp}{dl} = \frac{1}{1 + [G_s - \alpha(p - p_s)] \frac{p_0}{p}}, \quad (9)$$

where  $p_0$  – atmospheric pressure.

Under nonequilibrium conditions the equation describing the operation of perfect lift will be the following:

$$\frac{1}{\gamma_v} \frac{dp}{dl} = \frac{1}{1 + \left[ G_s - \alpha \left( p - p_s - \int_0^t F(t-\tau) \frac{dp}{d\tau} d\tau \right) \right] \frac{p_0}{p}}. \quad (10)$$

In perfect lift, the rate of pressure decline should be constant  $dp/d\tau = \delta = const$ . In our case, this can be the implementation of the requirements:

$$\frac{dl}{dt} = - \frac{\delta \cdot (1+W)}{\gamma_v} \quad (11)$$

In view of (11) the equation of nonequilibrium lift (10) can be rewritten as:

$$\frac{1}{\gamma_v} \frac{dp}{dl} = \frac{1}{1 + \frac{p_0}{p} \left[ G_s - \alpha \left( p - p_s + \delta \cdot \int_0^U F(t) dt \right) \right]}, \quad (12)$$

where:  $U = \frac{p_s - p}{\delta}$ .

Thus, the theoretical concepts allow to describe the pressure distribution in the fountain lift along the depth for cases of equilibrium and nonequilibrium lift.

### Numerical simulation of hydrogen sulfide seawater lift from given depth by gas-lift method

Dependence of pressure in the fountain lift from driving depth can be calculated using equation of perfect equilibrium fountain lift (9). The following value of parameters can be selected for calculations [5]:  $G_s = 7.0 \cdot 10^{-3} \text{ (m}^3/\text{m}^3\text{)}$ ;  $\alpha = 7.0 \cdot 10^{-4} \text{ MPa}^{-1}$ ;  $p_s = 0.1 \text{ MPa}$ ;  $H = 1000 \text{ m}$ ;  $\gamma_v = 10.0 \cdot 10^3 \text{ Pa m}^{-1}$ .

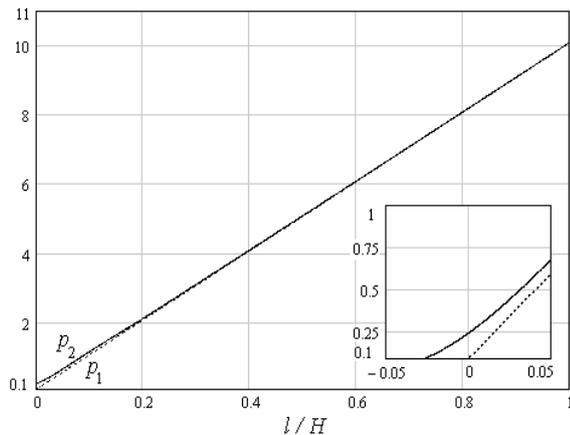


Fig. 5. Dependence of pressure  $p_1$  (MPa) in the sea and in the fountain lift  $p_2$  (MPa) from dimensionless depth  $l/H$ .

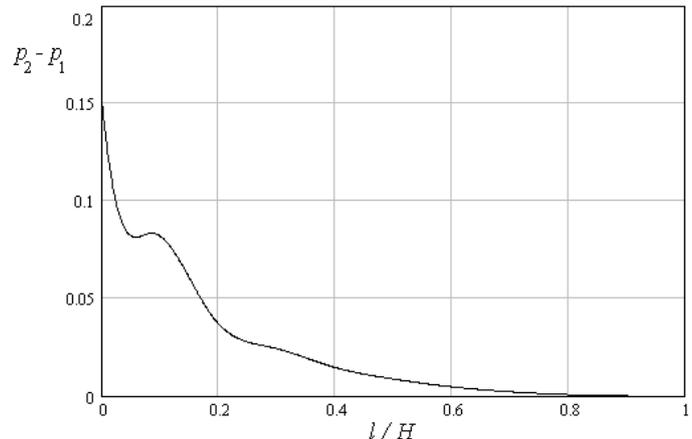


Fig. 6. Dependence of pressure drop in the sea and in the fountain lift  $\Delta p = p_2 - p_1$  from dimensionless depth  $l/H$ .

Fig. 5-6 provide the results of numerical solution of equation (9) and they show the dependence of pressure and pressure drop in open sea as well as inside the fountain lift from depth. From Fig. 5 it is clear that hysteretic dependence of pressure from depth of the fountain lift is observed with chosen lift parameters. In the open sea, pressure  $p_1$  changes from 0.1 MPa on the sea surface up to 10.1 MPa at the depth of 1000 m. Another picture of pressure dependence from depth is observed when fountain lift is filling with deep water with maximum composition of hydrogen sulfide ( $\sim 10 \text{ mg/l H}_2\text{S}$ ). In this case, liquid column in open sea is not compensated by pressure of gas-saturated water and, thus, there is a hysteretic dependence of pressure from depth (See insertion in Fig. 5). The “Coercive force” that corresponds to pressure difference in the lift and in the open sea, characterizes the fountain lift efficiency.

Numerical calculations of pressure drop at the sea level for the selected parameters (See Fig. 6) give a value of the order of 0.15 MPa which is equivalent to the height of water rise  $h = 15 \text{ m}$ .

Now, pressure dependence from depth can be considered under the same parameters that are used above, in nonequilibrium fountain lift. To do this, in equation (12) we specify a function of non-equilibrium in the form of  $F(t) = \exp(-t/t_0)$ . Missing parameters assume to be equal to:  $\delta = -0.1 \text{ MPa/min}$ ;  $t_0 = 0.3 \text{ min}$ .

Numerical calculations show that taking into account the nonequilibrium of the fountain lift leads to minor increase of pressure drop  $p_2 - p_1 = 0.16 \text{ MPa}$  and to increase of the lifting height of hydrogen sulfide water up to  $h = 16 \text{ m}$ .

Analysis of the performed calculations shows that the lift efficiency increases with the increase of thickness of non-hydrosulfuric layer near the sea surface and with increase of driving depth of the lower cut-off fountain lift [8].

### Mechanism for energetically efficient process to extract the hydrogen sulfide from the Black Sea water

A great number of patents are dedicated to the problem of energetically efficient process to extract hydrogen sulfide from the seawater. Two of them will be described as an example; their description is given in [5].

The essence of one of them is to place a vertical pipe at the necessary depth with polymer gas-permeable membrane selective to hydrogen sulfide which is pre-installed on the low end and the subsequent creation of the vacuum after the membrane. The membrane is oscillated due to energy of sea waves to intensify the process of hydrogen sulfide extraction. Partial pressure of hydrogen sulfide at the necessary depth reaches significant value and because of vacuum after membrane the hydrogen sulfide diffuses through its wall into the pipe and then it is compressed for further use.

The disadvantage of this method is the necessity to use mechanisms to create vacuum after membrane as well as decrease of hydrogen sulfide concentration in layers close to membrane which is caused by speed limit of hydrogen sulfide diffusion in deep layers. The latter circumstance causes poor efficiency of hydrogen sulfide extraction.

The second method of hydrogen sulfide extraction from seawater involves placing a vertical pipe into the seawater at the necessary depth, the transmission of water with hydrogen sulfide along the pipe and separation of hydrogen sulfide from water. Plates from activated aluminum, for example, are placed in the bottom part of the pipeline to create the gas-lift effect. The plate material partially decomposes water interacting with the seawater and emitting, herewith, hydrogen which rises upwards and draws water into the pipe. The extraction of the dissolved hydrogen sulfide starts because of pressure drop from the suspension moving towards the water surface, and it contributes to the effect of gas-lift.

The disadvantage of this method is the necessity to use activated plates that leads to rise in cost of the process of hydrogen sulfide extraction caused by the necessity of periodic change of spent plates. Moreover, hydrogen produced at water decomposition, reacts with impurities in the seawater that limits the gas-lift effect and, ultimately, causes small efficiency of hydrogen sulfide extraction from water.

The alternative towards the mentioned above methods of hydrogen sulfide extraction from the seawater is the method proposed by the authors of this article as well. The idea of the proposed method of hydrogen sulfide extraction should be taken from above section of numerical simulation. They allow to formulate basic requirements to energetically efficient method to extract hydrogen sulfide water from the given depths.

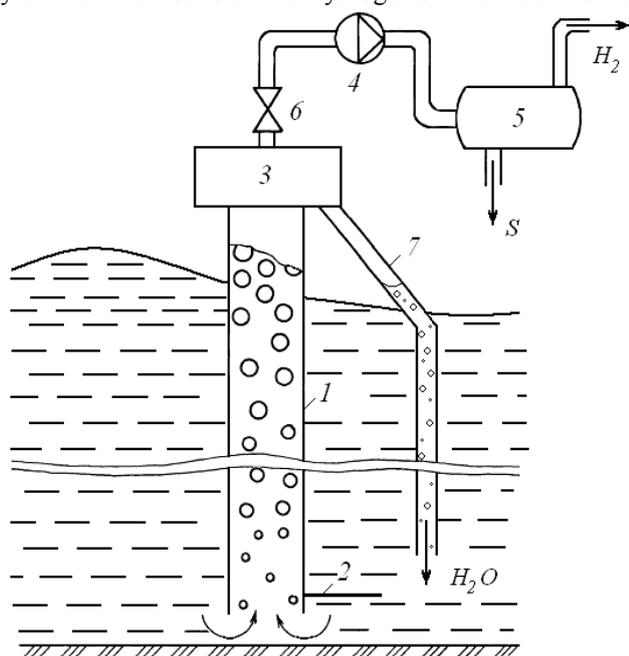


Fig. 7. The method to extract hydrogen sulfide from the Black Sea water.

The proposed above method to extract hydrogen sulfide from given depths is schematically shown in the Fig. 7 and is implemented as follows:

Vertical pipeline 1 is equipped with shutter 2 and placed into the seawater on the required depth. The cavity of the pipeline is free of water. Thereafter, the shutter 2 is opened and water enriched with hydrogen sulfide raises upwards by pipeline 1. As pressure raises upwards, and therefore, downwards, the higher water is the more saturated by hydrogen sulfide it gets, and it further vertical movement upwards is provided by the gas-lift effect. In the mechanism 3, hydrogen sulfide is separated from water and, using compressor 4, it is transferred to the mechanism 5 where it is decomposed on hydrogen and polymeric sulfur. Water purified from hydrogen sulfide is returned to the sea through the branch pipe.

Efficiency of this mechanism is determined by the cross-sectional area of the pipeline, depth of it immersion in the sea and height of lift of the lower level of the mechanism 3 (height of lift of hydrogen sulfide water in the pipeline). According to numerical calculations, the efficiency of the machine will make not less than 20 l/min of hydrogen sulfide [5] upon condition that

50% of hydrogen sulfide emission from the seawater.

Thus, the machine described above to extract hydrogen sulfide from the given depths allows in a manageable way and without energy costs to deliver water, enriched by hydrogen sulfide, to a sufficient height where it will be sequentially degassed and then undergo potential and heat energy by known methods [9].

The obtained hydrogen can be used as ecologically pure fuel and polymeric sulfur - as raw materials for the chemical industry. The return water with residual composition of hydrogen sulfide should be directed to the sea at the depth where the concentration of hydrogen sulfide in the return and sea water are the same.

#### Experimental simulation of energetically efficient method to extract hydrogen sulfide from the Black Sea

The method described above to lift the hydrogen sulfide from water with gas-saturation of 10 mg/l, that equal to depths of the Black Sea of 1000 m was implemented in simulation experiment.

The machine, scheme of which is given in the Fig. 8, allowed simulating the gas-saturation of water at the necessary level.

Air was used instead of hydrogen sulfide in experiment. The pump 5 through T-socket 4 produced the overpressure in the capillary with internal diameter of 0.02 m which led to the emergency of regular sequence of bubbles (Fig. 9). The size of air bubbles and the resulting gas-saturation were estimated visually using line-up. In the Fig. 9 one can see the meniscus that was raised to the level of water in the tank 1 in the capillary 3 and two air bubbles moving in the capillary.

Experiments showed that the height of gas-saturated water lift was 0.01-0.015 m when the length of capillary 3 was 1 m. The obtained result could be converted using the principle of similarity to estimate the water lift in a full-scale facility. In this case, the value of its lift in the pipe equal to 10-15 m could be obtained under condition of complete water degassing which is observed in this experiment. This value quantitatively corresponds to the result of numerical

simulation given in the above section.

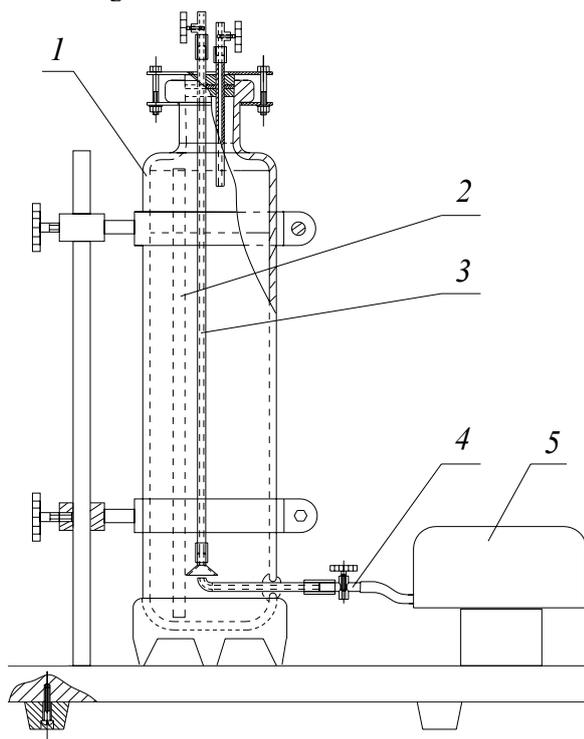


Fig. 8. Scheme of the facility for simulation of water gas-lift: 1 – glass vessel; 2 – ruler; 3 – capillary; 4 – T-adaptor; 5 – pump.

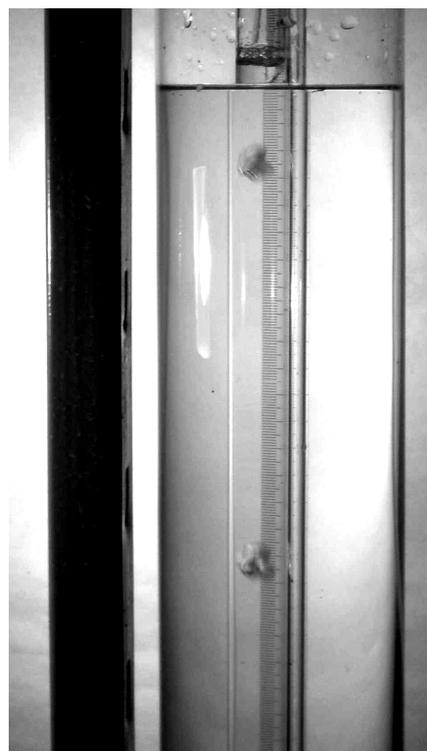


Fig. 9. Fragment of the facility during simulation of air-saturated water lift.

Thus, possibility to lift the gas-saturated water is demonstrated in this model experiment and this is an encouraging factor in solving the problem of energetically efficient method to extract the hydrogen sulfide from the Black Sea water.

## ALTERNATIVE ENERGY OF HYDROGEN SULFIDE WATER OF THE BLACK SEA AND THE BLACK SEA REGION

### Stimulus and basic elements for the development of hydrogen sulfide energy of the Black Sea Region

Stimulus for the development of the RES-based energy industry is an anticipation of depletion of traditional energy-producing materials and environmental degradation as a result of traditional energy functioning [10].

RES-based energy industry is the most dynamic and perspective sector of the global energy industry which solves a number of problems of depletion of traditional organic energy resources but also contributes to environmental safety. The most obvious areas of RES development are:

- Hydrogen energy;
- Wind;
- Solar;
- Geothermal;
- Hydroenergy (large and small);
- Bioenergy;
- Energy based on hydrogen sulfide dissolved in the seawater or being in the gas phase of mud volcanoes;
- Environmental energy (secondary resources such as municipal solid wastes (MSW), differences in salinity of sea and fresh water).

Predictions of global energy development in the coming decade are that in 2040 50% of electricity will be produced from RES, including in Ukraine – at least 30%. In particular, it will be stimulated by the Law of Ukraine “On Alternative Energy Sources” (No. 555-IV of 23/02/03), as well as programs and legal documents developed on its basis.

The Black Sea Region, in this respect, is the most promising because here together with existing traditional renewable energy resources there is almost inexhaustible reserve of hydrogen sulfide which is not much inferior to the energy value of natural gas. Naturally, a comprehensive study of the problem of complex energy extraction from all existing sources of the Black Sea and Near Black Sea Region is of great interest.

Search of optimal methods to use it in relation to specifics of the Near Black Sea Region is an important problem. The following description will focus on types of energy storage contained in the Black Sea and Black sea Region, as well as how it could be recycled.

### Hydrogen sulfide energy sources

The Black Sea is not the only one water pond on our planet waters of which are full of hydrogen sulfide. Hydrogen sulfide is also in waters of Cariaco basin, Red Sea, near the Peru coast, Namibia, in some deep fjords of Norway. The Red Sea waters have one of the biggest concentrations of this gas; however, the Black Sea has the first place among the above listed regions on weight of the hydrogen sulfide dissolved in its waters.

Until recently, there was an opinion that it is unreasonable to extract hydrogen sulfide from the Black Sea water due to its unpredictable ecological consequences and small energy efficiency of the expected effect because of low level of the hydrogen sulfide concentration. The hydrogen sulfide is absent in surface layer of 100-150 m thickness of the Black Sea. Its concentration increases with the increase of depth and becomes maximal at the bottom of the Black Sea which is of the order of  $\sim 10$  mg/l [3].

However, a closer study of the problem of depositing the Black Sea hydrogen sulfide showed that the possibility to obtain hydrogen sulfide from the depths of the Black Sea based on the latest technological developments that allow to extract the hydrogen sulfide water spending minimal energy on its rise in an ecologically safe manner [11] and providing the optimal conditions of extraction the gaseous hydrogen sulfide from sea water [12].

Electricity could be produced from the obtained hydrogen sulfide directly using high-temperature solid oxide fuel elements or decompose it into polymeric sulfur and hydrogen which naturally will require additional costs for hydrogen sulfide decomposition.

If annually extract about 25 million tones of hydrogen sulfide from the Black Sea it would be equal to obtaining energy of about 9.25 billion of kilowatt-hours (one kilogram of hydrogen sulfide generates 1334 kJ when it is burnt). This rate is 10.4% from the level of electricity production on NPPs of Ukraine (88.782 billion of kilowatt-hours in 2005). Thus, the Black Sea as a source of hydrogen sulfide could provide an essential contribution to the energy balance of Ukraine [3].

To have such a contribution it is necessary to solve a problem of energy efficient delivery of hydrogen sulfide to the sea surface.

The authors of this article [5] proposed a solution to this problem using natural gas-saturation of the Black Sea water.

Hydrogen sulfide extracted in such a way is sent immediately to obtain electricity directly in high-temperature solid-oxide fuel element or to be decomposed into hydrogen and sulfur.

### Specific hydroelectric resources of the Black Sea

Hydroelectric resources proposed for conversion into electricity are of specific nature: they could be acquired only by the rise of hydrogen sulfide water to a given height of technology. [5].

The height difference generated due to gas lift could be effectively converted into electricity using hydraulic turbines. The hydraulic turbine converts the energy of under pressure water into mechanical energy of rod rotation. Tidal hydroelectric hydropower plant (THP) can be used as the prototype. However, unlike THP which always operate with variable pressure, the proposed power plant will operate with constant pressure drop.

Parameters of THP that are going to be constructed in Russia in Tugursky and Penzhinsky Bay of the Okhotsk Sea and in Shantar Islands where the tide height is 13 m [10] could be compared with their parameters to assess the effectiveness of hydropower station on the return hydrogen sulfide water.

As it was mentioned in [5, 13], height drop may reach 13-15 m when hydrogen sulfide water is extracted. Use of micro hydropower plant with propeller wheel with force equal to 4.0-10.0 m, area of an intake machine of 0.45 m<sup>2</sup> and flow of 10-0.21 m<sup>3</sup>/s can provide electricity with power up to 10 kW.

### Technologies for conversion of the Black Sea thermal energy

Since the Black Sea is giant heat storage of solar energy, it is possible to use its heat. One of the technologies to obtain electric power from thermal energy of the Black Sea is OTEC technology (abbr. from Ocean Thermal Energy Conversion) [9].

OTEC works best when temperatures drop between the warmer upper layer of the ocean and colder deep ocean water is 20°C. In the Black Sea Region this ratio is lower and is equal to 15-16°C near the border coast between Russia and Georgia and 14.5-15°C near the Eastern coast of the Crimea. At such a temperature difference, there are several ways to use different types of technologies OTEC.

**Closed-cycle technology.** This technology uses liquid with low boiling point such as ammonia which rotates the turbine to produce the electric power. Warm surface seawater evaporated the liquid with low boiling point passing through thermal exchanger. The expanding steam turns the turbine located on the same shaft with electric generator and cold "deep seawater" condensates the spent steam back to liquid passing through the second thermal exchanger.

In 1999, the Natural Energy Laboratory commissioned a 250 kW pilot closed-cycle OTEC which is the largest operating power plant ever commissioned.

**Open-cycle technology.** The closed-cycle technology uses the warm surface water of tropical oceans to produce electricity. The technology includes the following: warm seawater goes to low pressure tank and boils. The expanding steam turns the low pressure turbine connected to the electric generator. Steam, which is almost distilled water, is con-

densed back to water again by cold deep ocean water.

**Hybrid technology.** This technology combines features of technologies of opened and closed cycles. In this hybrid system the warm seawater goes to vacuum tank where it is converted into steam like in the open-cycle technology. The water steam evaporated liquid with low boiling point the steam of which makes turbine to produce electric power.

Among the mentioned above technologies the advantage of OTEC open or hybrid technologies is clear, because there is production of electricity and fresh water. Theoretically, such technologies as OTEC allow to produce up to 2 MW of electric power and to obtain daily up to 4300 m<sup>3</sup> of distilled water.

Thus, despite the fact that the Black Sea Region is not the tropical, the temperature drop of seawater is enough to use OTEC technologies designing HSEGC.

### **The salinity energy gradient of the Black Sea**

The most promising methods to utilize the salinity energy gradient are based on use of osmotic pressure. Thence, they often talk about the energy of the salinity gradient, as osmosis energy [14].

The osmosis phenomenon is the following. If we take a semi permeable membrane and place it as a partition in a vessel between fresh and salt water (semi-permeable membrane - partition, which transmits fresh molecules in half of the vessel filled with salt water and salt molecules in the membrane does not miss half of the vessel with fresh water), the osmotic forces will deliver fresh water to salt water. Because of this the membrane is called semi permeable. Energy generated during this process appears in the form of high pressure that occurs in the part of the vessel with salt water. This is called the osmotic pressure (sometimes called osmotic waterfall). High pressure generated in the half of the vessel with salt water balances osmotic forces that displace fresh water molecules into salt water through semi permeable membrane.

It is necessary to have a source with lower concentration near the concentrated salt solution to obtain the osmotic energy. In the oceans such sources are the mouth of the rivers flowing into it. In the Black Sea this could be difference between salinity of deep (more than 1500 m) and upper layers (less than 50 m) of the sea that reaches values of 5-6 ‰. Such salinity drop can provide osmotic pressure of 0.3° MPa, which equal to the salt water rise up to 30 m height.

The salinity gradient energy, calculated from the osmotic pressure, is not subject to restrictions on the efficiency related to the Carnot cycle. This is one of the positive features of this type of energy. The problem is how best to convert this kind of energy into electricity.

Practical implementation of osmotic converters is possible in the nearest time. Thus, the largest Norwegian electricity concern Statkraft builds world's first osmotic power plant.

For the Black Sea the osmotic water rise to the height up to 30 m will allow to obtain up to 100 kW of electricity from the area of 1 m<sup>2</sup> during the operation of micro hydropower plant MHPP-100 K, for example. Thermal power obtained herewith from direct burn of hydrogen sulfide will be ~ 80 kW.

### **Wind waves and swell of the Black Sea**

Wind waves and swell are common everywhere on open surfaces of water of small reservoirs as well in the vast oceans and seas.

Wind waves are called surface waves caused when the wind stops and the water is covered with swell the height of which is gradually disappears. The height of wave or swell is called a vertical distance that separates the cavity wave from its crest.

The first theory of surface waves was proposed by Mr. Gerstner, the Professor of Prague University, in 1802. However, it referred to swirling motion of water and did not determine the maximal possible height of the wave. Much later, Kelvin and Helmholtz independently performed works to explain the instability of surface water under wind influence [15, 16].

In these works it was shown that the wind waves occur due to instability development [17] which later was called "Kelvin-Helmholtz instability". Such waves can accumulate huge amounts of energy. In addition, these waves can be characterized by quite unusual behavior of their amplitudes: they can grow in size in a very short period of time in an explosive manner. [18].

It is necessary to determine basic parameters of waves and swells that are inherent to the Black Sea to evaluate the effectiveness of the wave power plant in the Black Sea Region.

First, about maximal values of the wave parameters that should be used when designing the wave power plants.

Thus, the biggest height of the Black Sea waves was 14 m and length – 200 m. The unique wave was recorded by stationary buoy near Gelendzhik coast in 2001. Its height was above the background height of waves of 2-2.5 m in 3.9 times, and the wave length of the order of height. Herewith, typical lifetime of such formation is only 4-5 sec (during this time the wave runs 20 m).

According to a special nine-point scale of the sea surface it is assumed that 1 point of excitement corresponds to a wave height of 25 cm, 2 points – 25-75 cm, 3 points – 75-125 cm etc.

Estimation of average power of the wave power plant is performed based on average wave parameters.

Average annual wave height in the Black Sea in 2003 was 90-100 cm based on wave station DATAWELL data.

Hence, in the North-Western Pacific Ocean the average wave height is about 1.25 m, the power of wave power plant is about 75 kW/m, the similar power obtained from the Black Sea waves with length not more than 20 m will be about 25 kW/m.

The advantage of this method to generate energy is that one should not look for special places with specifically favorable geographic conditions, unlike tidal stations, to use energy of wind waves and swell. Waves and swell are in any area. Besides, one should not construct big and costly dams to use energy of wind waves (and swell).

### Solar energy of Crimea

Solar radiation flux that passes through an area of  $1 \text{ m}^2$  and located perpendicular to the radiation flux at a distance of one astronomical unit from the Sun centre is  $1367 \text{ W/m}^2$  (solar constant). Maximal flux of solar radiation at the sea level is  $1020 \text{ W/m}^2$  due to absorption of the Earth's atmosphere. According to other reference data [19] the real solar radiation flux of Earth is about 1 kW per meter square. Note, however, that the daily average solar radiation flux per unit area is at least three times smaller (because of the change of day and night and change the angle of the sun above the horizon). This value is half as much during winter in temperate latitudes. Besides, the prospects to develop solar energy also reduce because of global dimming caused by human-induced decrease in solar radiation reaching the Earth's surface.

The mentioned above quantity of energy from unit of area defines possibilities of solar energy.

The main contribution to the density of the solar radiation flux falls on the visible and infrared radiation, as contribution to the solar radiation flux with wavelength bigger than  $2.5 \mu\text{m}$  is negligible [19].

Herewith, the share of direct solar radiation is: from November till February is 20-40%; from March till October – 40-65%. On the Southern coast of the Crimea in the summer months – up to 65 – 70%.

The Crimea has also the biggest number of solar days during the year (290-300 days per year) that creates energetically favorable and cost-efficient situation for wide practical use of solar energy.

The main technological methods to use the solar energy are: photovoltaic conversion of solar energy into electrical energy or generating the heat energy for heating buildings (mirror hub, water heater, and thermal hub).

Below we will briefly discuss the specific application of these techniques.

**Photovoltaic converter of solar energy.** Present production of photocells is almost entirely based on silicon. Prospective application of silicon photovoltaic of solar energy is due to their environmental performance, significant PV service life (over 25 years at average rate of degradation of the photoelectric properties of the battery of 1% per year) and low maintenance costs. About 80% of all modules is produced using poly or single crystal silicon and the rest 20% use amorphous silicon.

Solar batteries from amorphous silicon have their own distinctive and unique features: high efficiency of solar energy conversion into electrical energy (up to 10%); low cost of the obtained electricity 10-12 cent/(kilowatt-hours); low weight per unit of capacity; resistance to mechanical damage (hit, bend and damage effect such as shot or shrapnel damage).

The capacity of photovoltaic converters of solar energy that are currently implemented in the Crimea by 2010 planned be up to 3.0 MW which will provide fuel saving up to 1.7 thousand tones of conventional fuel in independent power supply systems [20] (thermal value of conventional fuel is 29.33 MJ/kg).

Currently, there is an increasing capacity of solar power plants of Crimea. If 7.5 MW was in operation in the first half of 2011, then by the first half of 2012 there were more than 219 MW in operation that corresponds to 7% of the energy consumed in Autonomous Republic of Crimea [21].

Efficiency of photovoltaic converters could be estimated based on solar energy rates reaching ground in the Crimean region. The annual average daily solar radiation power in the Crimea (about  $45^\circ\text{C}$  of North Latitude) is estimated by value of  $448.6 \text{ W/m}^2$  [22]. When conversion efficiency is 10-14%, then, 44.8-62.8 W of electric power could be obtained from  $1 \text{ m}^2$  of photovoltaic converter. The power obtained from one square meter will allow to save 132 kg of conventional fuel per year.

**Mirror converter.** The operation principle of mirror converter is to focus solar rays, for example, using a concave mirror. Mirror is a main part of solar concentrator, a device where parallel solar rays are collected inside a concave mirror and are directed to the vessel with an effective absorber, for example, water. Mirrors used in machines are traditional, made of glass, or from polished aluminum.

Thermal power of mirror concentrator is determined by quantity of solar radiation, working absorption surface and its thermal efficiency (typically 20-50%). So, for example, with power flow of solar radiation of order of  $850 \text{ W/m}^2$  the efficiency of thermal conversion is 30% and absorption area of order of  $1.25 \text{ m}^2$  it is possible to obtain 320 W of thermal power or 260 W of electric power (with 80% efficiency of thermal power conversion into electric power in steam turbines).

**Water heater.** Another promising direction of solar power engineering is: direct irradiation of thermal energy for heating the buildings. Average annual density of solar energy flow in Ukraine is 180-250  $\text{W/m}^2$  (in the Crimea this ratio is higher in 1.5-2.5 times). This energy is enough to heat 100-120 liters of water from one square meter up to the temperature of  $45\text{-}55^\circ\text{C}$ .

Large number of sunny days in the Crimea (290-300) makes a perfect perspective to use solar collectors. Consid-

ering the predicted growth of prices on energy resources and environmental cleanliness of the obtained energy, the use of solar energy is very profitable. The proposed systems are more effective on sites the thermal supply and hot water supply of which is done from boiler houses that use liquid fuel (heating oil, fuel oil, diesel fuel). Maximum effect is achieved at the resort - recreational facilities, where the peak of hot water demand coincides with the maximum number of hours of sunshine per day. The proposed solar systems work reliably together with automated boiler houses due to the perfect system of automated control. Daily energy production at the 50th latitude is about 2kW-hour from the meter square. The temperature in the tank-battery reaches 60.....70 degrees. The facility efficiency is 40 %.

**Thermal concentrator.** Thermal concentrator – is the capacity of different geometry made of thermal isolating material, one side of it is covered by a single or double glass. A corrugated metal plate is installed inside the box for maximal absorption of sun rays. Heated air or water inside the box periodically or continuously are withdrawn by a fan or a pump.

### Wind energy of the Crimea

Average annual, winds of Northern horizon dominate in the Crimea, they are of relatively small power (less than 6 m per second or 2 points, Beaufort).

The biggest speed during heavy storms is 20 meters per second and more, and at high altitudes above Yalta reaches up to 40 meters per second.

With the increase of height the wind speed also increases in 2-2.5 times, and, therefore, the value of generated energy. Thus, it is very important for Ukraine to develop wind energy conversion technologies at altitudes above 50-100 m with maximal efficiency and it can also increase the efficiency of HSEGC.

The use of a simple formula to calculate electricity generated by wind power plant created on the basis of low speed turbine, wind concentrator, output device for optimal modes of wind passing through the turbine, as well as new constructional materials, allow to increase efficiency up to 50-55% [23]. Thus, the quantity of the obtained electricity increases up to 8-15.6 times per unit of the swept surface by increasing the selection height of the wind energy, as well as increase of efficiency of wind turbine in 2-2.5 times.

Calculations show that use of high-altitude wind energy (100 m and higher) may increase energy balance of the Crimean Region up to 70 W per 1 m<sup>2</sup> of the swept surface.

### Energy of deep heat flow of the Earth

In the Crimea it is possible to use energy of deep heat flow of the Earth. Typically, the temperature in mines increases on 25-30°C with every kilometer of depth. The background values of the deep heat flow are about 44 mW/m<sup>2</sup> in the most parts of Ukrainian shield, and in the areas of anomalies they reach values of 70-90 mW/m<sup>2</sup>, and in some cases even up to 130 mW/m<sup>2</sup>. Such areas are recorded in the Crimea as well. Economic estimations indicate cost effectiveness of geo-energy resources for heat supply with minimal geothermal gradient of 0.02-0.025 C/m, where C – heat capacity per unit volume of geological material equal to 2.5 mJ/m<sup>3</sup> [24].

### Energy of human waste

Energy power of constantly renewable municipal solid wastes (MSW) is particularly important for the Crimea considering uniquely high requirements to ecology in this region where in 2007 it was accumulated about 1 million tones [25] according to official data. The most pure way of processing this quantity of MSW is “Thermoselect” on which Japan already has 7 plants, the first of which was started in 1998. This technology does not pollute the atmosphere and does not form secondary wastes – everything is converted into synthesis gas and other useful products [25]. One tone of MSW produces 1090 kW/t of energy, part of it goes for internal needs of production, at 750 kW/t goes for external consumption. And besides, this technology can be used for processing of almost all types of toxic wastes (except for radioactive wastes) including up to 20% of liquid wastes which is very important for the Crimea.

### Accumulation of energy

Currently, expensive pumped storage systems are constructed to compensate daily fluctuations of electricity consumption generated by nuclear power plants (NPPs), thermal power plants (TPPs), and they are often associated with flooding the effective areas and cause ecological imbalance. Some renewable energy sources (wind, solar) are exposed to daily and seasonal fluctuations. Such methods as electrolysis of water for hydrogen production are already used to accumulate energy of these sources. Therefore, there is still an important problem of development economically effective and environmentally sound technologies to accumulate energy of big power that is equal to power of pumped storage facilities.

### SUMMARY

As it was noted earlier, the mentioned above complex extraction of the renewable energy sources from hydrogen sulfide area of the Black Sea and the Black Sea Region could not only increase significantly the energy balance of the Crimea but also contribute to social and economic development of the region.

This is confirmed by the Fig. 10 and the bar chart in it that describes absolute values of specific contribution of



