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THE DIFFICULTIES OF THE EXTRACTION OF HYDROGEN SULFIDE FROM THE BLACK SEA WATER AND METHODS TO OVERCOME THEM

ТРУДНОСТИ ИЗВЛЕЧЕНИЯ СЕРОВОДОРОДА ИЗ ВОД ЧЕРНОГО МОРЯ И МЕТОДЫ ИХ ПРЕОДОЛЕНИЯ

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Abstract. Among the alternative energy sources, of particular importance is the hydrogen energy industry, whose advantage over petroleum products consists in its high environmental safety and caloric content, inexhaustible natural reserves, its use in the internal combustion engines, and so on.

Among the hydrogen–containing raw materials used in the fuel elements, particular attention is paid to hydrogen sulfide, which is disintegrated into sulfur and hydrogen. One of the biggest sources of hydrogen sulfide is the Black Sea, whose total volume is increasing annually by 4–9 million tons.

The paper dwells on several methods for extracting hydrogen sulfide from the Black Sea basin, as well as associated difficulties. It also presents methods for the decomposition of hydrogen sulfide, of which special mention should be made on the plasma–chemical membrane technology.

Аннотация. Среди источников альтернативной энергии, особенное значение придается водородной энергетике, чье преимущество по сравнению с нефтепродуктами заключается в высокой калорийности и экологической безопасности, в неисчерпаемых природных запасах, в возможности использования в двигателях внутреннего сгорания и т. д.

Среди видов водородосодержащего сырья, используемого в топливных элементах, особенное внимание привлекает сероводород, который распадается на серу и водород. В качестве одного из самых крупных источников происхождения сероводорода рассматривается Черное море, в котором его общее содержание ежегодно увеличивается на 4–9 миллионов тонн.

В работе рассматривается несколько методов извлечения сероводорода из бассейна Черного моря, а также связанные с этим трудности. Также в ней представлены методы разложения сероводорода, из которых особенно нужно отметить плазмохимическую мембранную технологию.

Keywords: hydrogen energy industry, hydrogen sulfide decomposition, membrane technology.

Ключевые слова: водородная энергетика, распад сероводорода, мембранная технология.

In recent decades, the intensive development of a modern energy sector and transport leads humankind to a global environmental disaster, with a daily reduction in reserves of fossil fuel. Therefore, in order to avoid the energy crisis in the nearest future, the problem of search for a new non-traditional energy source is of high importance for both the energy industry and the domestic sector.

Among the alternative energy sources, of particular importance is the hydrogen energy industry, whose undeniable advantage over petroleumil products consists in its high environmental safety and caloric content, its use in the internal combustion engines, and so on. Therefore, along with other alternative sources, the prospects of hydrogen use in motor transport are now being actively considered. Since 2014, mass production of cars running on hydrogen has started in Japan by two big companies Toyota and Honda.

It is noteworthy that combustion products of the internal combustion engines do not not containe at all environmental pollutants, such as carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbons (C_xH_y) and solid particles. However, the main environmental problem in these types of engines is the minimization of nitrogen oxides (mostly NO) in combustion products, which are created as a result of oxidation of nitrogen molecules at high temperatures.

Among the hydrogen-containing raw materials used in the fuel elements, particular attention is paid to hydrogen sulfide (H_2S), which is an extremly poisonous and explosive substance. Its maximum concentration in the air in human settlements is 0.008 mg/m^3, and the poisoning dose is 0,05-0,07 mg/m^3.

From the energy standpoint, 1 m^3 hydrogen sulfide is equivalent to 1,49 m^3 of natural gas and is burning in excess oxygen as a result of the following reaction

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

It is known that every million tons of hydrogen sulfide allows for producing 940 thousand tons of pure sulfur and 60 thousand tons of hydrogen, which, by calorific capacity, is equivalent to 250 thousand tons of oil.

Today, the focus of attention from science is the Black Sea basin, since its deep waters contain large amounts of hydrogen sulfide, whose sources of origin are gases erupted from volcanoes existing in the seabed area and from geological fissures. Between the hydro-sulfuric and aerobic layers existing in the Black Sea, there is formed a layer containing simultaneously transition oxygen and hydrogen sulfide, where the intensive and multi-stage oxidation occurs as a result of the reducing reactions large amounts of sulfur-contain compounds are created.

On the basis of the monitoring, the Black Sea is considered to be one of the biggest sources of hydrogen sulfide, whose total volume is increasing annually by 4-9 million tons. Such a large concentration of hydrogen sulfide in the sea may lead to the large environmental disaster in a few decades, since currently, only its top 100-150 m layer contains oxygen, and the lower layers are saturated with hydrogen sulfide. That is, the Black Sea is not only a serious environmental problem, but it can become a potential source of the hydrogen energy industry.

Gaseous hydrogen sulfide extracted from the Black Sea is used as a rare natural material for obtaining future fuel: hydrogen, sulfur, sulfuric acid and other sulfur-containing compounds, but when removing gases, is the main problem is the transition of gases dissolved in water on the surface to gaseous state, and their complete separation from sea water.

There are several methods for separating hydrogen sulfide from the Black Sea water:

- The electrohydraulic shock is carried out at a specified technological height, which ensures separation of hydrogen sulfide, while cleaned water returns into the sea;

- As a result of action of UV radiation with a certain a wavelength (180-253 nm), hydrogen sulfide is dissociated selectively into hydrogen and sulfur;

- Method of H_2S sseparation with the use of ozone is based on the technology used for purification of wastewater and reservoirs water from sulfur, during which H_2S existing in water is oxidized in the ionized air, and water and sulfur are formed;

- Additional treatment of hydrogen sulfide-containing waters with mineral acids containing water and further aeration, during which energy is produced by H_2S oxidation;

- The method of extraction of hydrogen sulfide from deep waters using a normal pipeline and its division into the elements is based on the extraction of H_2S-containing water from the depths, which is due to the difference between the air pressures existing the sea surface and the air pressure in the receiving area;

- After the primary pumping of water by means of a vertical channel pump, it is possible to obtain the gas-liquid fountain in the sea from the difference between the hydrostatic pressure at the level of the channel's receiving section, and pressure of the gas-liquid mixture existing inside the channel at the same level — using the gas-lift effect without use of energy.

Of the above listed methods for extracting gaseous hydrogen sulfide from the deep-sea water, the most effective and efficient are methods using a solid vertical channel or pipeline equipped with pump. However, the main problem is the further effective division of gas mixtures extracted from the sea depth with maximum energy-saving.

Direct disintegration for obtaining sulfur and hydrogen, is based on the use of the technologies of phyto-catalytic, electrolytic, electro-plasmic and plasmo-chemical separation. The phyto-catalytic method is characterized by lower energy use, but due to the duration of the process, it is unacceptable for large-scale technologies. The electrolytic method is widely known, although it is distinguished by high energy expenditure. The electro-plasmic method involves the use of plasma flow, which is formed in the electronic plasmatron, but the design of the modern plasma reactors need to be refined from the energy and commercial standpoints.

The plasmo-chemical membrane technologies widespread at the current stage deserve attention, which is due to the effectiveness, selectivity, continuity, simplicity and low energy inputs of these separation technologies, and so on. For instance, obtaining of 1 m^3 of hydrogen in the industrial equipment requires 1 kWh of energy inputs, while obtaining the same amount of hydrogen by electrolytic method requires 4,5 kWh of energy.

The membrane technology of separation of substances is intensively developed and applied in different industries, including: extraction of helium from natural gas; air enrichment with oxygen; in the oil refining process for the extraction of hydrogen, helium and ammonia from natural and technological gases; for separation of high-molecular substances from solutions containing low-molecular impurities; in concentrating solutions and purification of gases, and so on.

When solving the problem of separation of gaseous hydrogen sulfide from the Black Sea water, it is necessary to take into account the form of the existence of divalent sulfur in the sea water, because sulfur in water can be in the form of H_2S^0 or HS^- and S^{2-} ions The ratio of these two forms is determined by pH value of the sea water hydrogen (pH in the deep waters of the Black Sea depends on H_2S^0- and its value decreases to 7,6). When the hydrogen value pH> 10, then the content of S^{2-} ions can be neglected. When pH = 7, then the compositions of H_2S^0 და HS^- are almost the same, and when pH = 4, sulfur is represented in the form of H_2S^0 of almost completely non-dissociated molecule.

Only 15% of the total divalent sulfur in the Black Sea water is present in the form of H_2S^0, while the rest is represented as chemical compounds of heavy metal sulfides, so the possibility of transition to gesous state is complicated.

For the purpose of carrying out the studies proceeding from this, the use of thermodynamic modeling allows us for assessing the chemical form of divalent sulfur content in the Black Sea water with the dependence on the variation of the temperature and pressure. (Calculation was carried out on 18% and 22% salinity, when pH = 8,2). The calculation results are illustrated in Figures 1, 2, and 3.

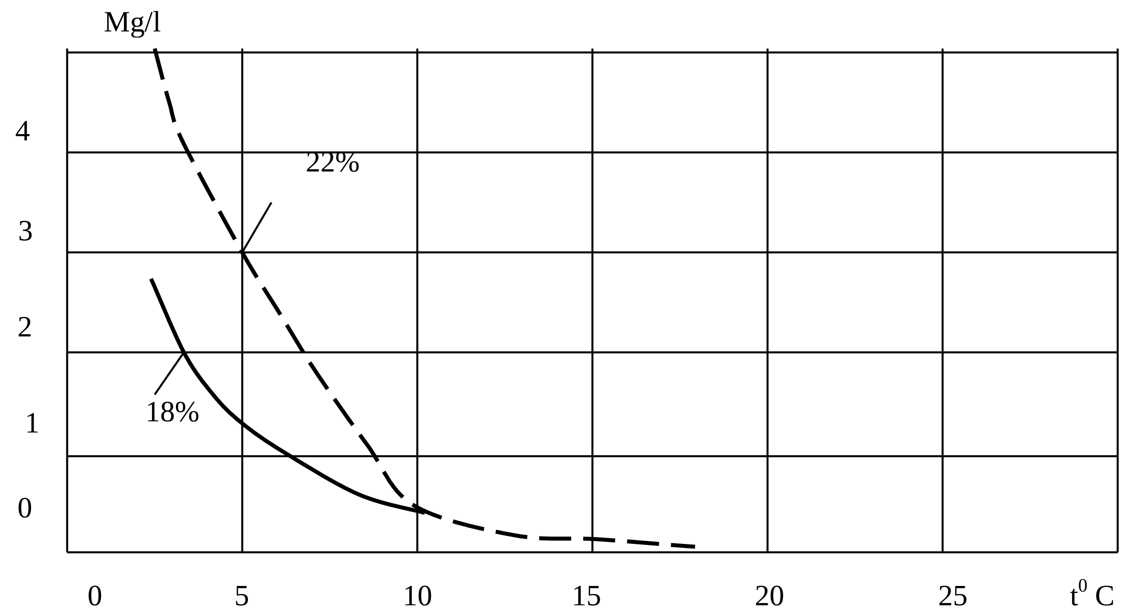

Figure 1. The relationship between the divalent silfur concentration
in the sea surface water and the temperature P=10^5 Pa.

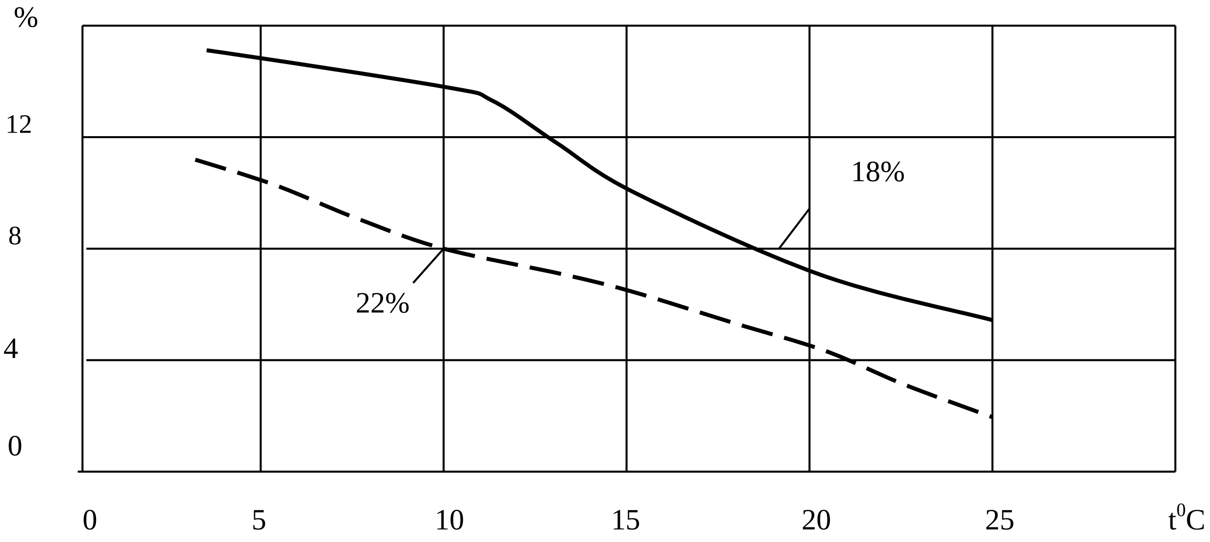

Figure 2. The relationship between the percentage of H_2S
in the sea water and the temperature P=10^5 Pa.

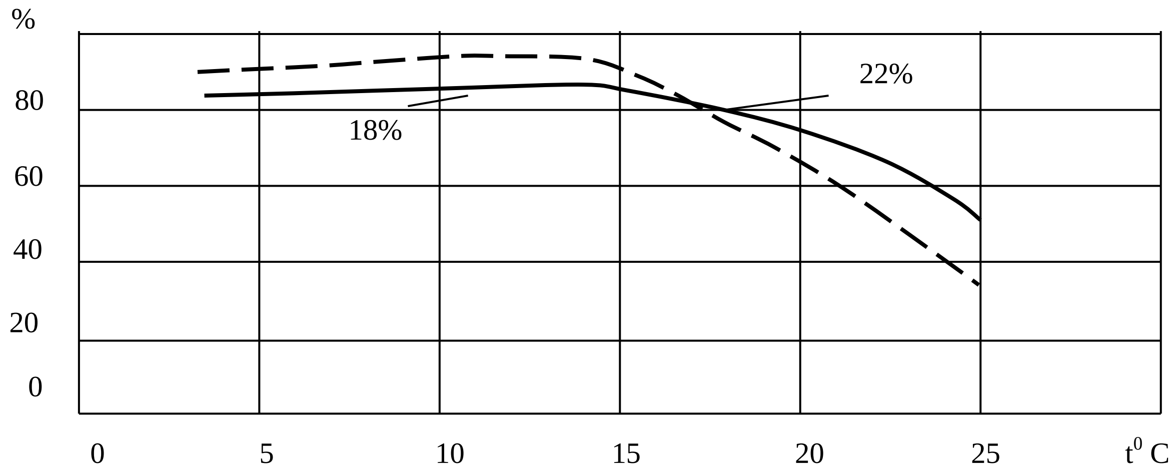

Figure 3. The relationship between the percentage of HS^-
in the sea water and the temperature P=10^5 Pa.

The results of the calculation demonstrate that in all physical-chemical conditions under consideration, the major part of divalent sulfur is present in the form of heavy metal sulfides dissolved in HS or water. In addition, by the increase in the salinity and decrease in the temperature by diatomic sulfur, the total concentration is increased (Figure 1), and the increase in the salinity and the increase in the temperature, the share of H_2S^0 goes down (Figure 2). As to HS^-, its concentration increases by the increase in the salinity and the decrease in the temperature Figure 3).

That is, the difficulty of obtaining hydrogen sulfide consists in the presence of its major part in the Black Sea water in the form of an aqueous solution. Therefore, the method of extraction of hydrogen sulfide in the gaseous form can be broken down into two groups: the extraction of hydrogen sulfide from the deep-sea water up to the sea surface, or hydrogen sulfide in the gaseous form directly at the place of its extraction.

The main problem in the extraction of gases from the sea depth is the increase in the level of water containing dissolved gases, the transition of gases dissolved in water on the surface in gaseous state, and their complete separation from the sea water. It is also important to avoid the mixing of the surface layers of gases remaining in solution with water, to eliminate their negative impact on the atmosphere.

During the recent period, the membrane methods of for the separation of gaseous mixtures have been developed rapidly, which allows for separating hydrogen sulfide from the sea water directly in the deep-sea water. In this regard, particular attention should be paid to methods of ion exchange and selective absorption in polymeric membrane. These method are based on the property of semi-permeable hydrophobic membrane to carry the gas and retain water.

Separation of hydrogen sulfide from sea water can by the membrane technology is possible using the submersed pipeline device, which provides filtration with hydrophobic membrane. At this time, it is possible to obtain hydrogen sulfide in the membrane volume in the gaseous form, will be extracted to the surface through the pipeline.

In terms of use, membranes are classified as microfiltration, inverse-filtration, reverse-osmotic, electrolytic and dialysis membranes. The membrane separation of mixtures is based on the use of porous, non-porous, asymmetrical and composite selective membranes. Transport of their gases is carried out by different mechanisms, of which most attention should be attached to molecular diffusion, whose determining factor is represented by the difference between the concentrations on both sides of the membrane.

The main characteristics of membranes used in the membrane technology are selectivity, conductance and durability, due to which a significant defining feature is membrane's substance. Both inorganic substances (metal wires, ceramics, ceramic metal, glass, graphite) and polymers (fluorine plastic, celluloses, acetates, polyethylene, etc.) are used to make membranes.

In response to the growing demand for hydrogen in the future, more and more studies focus on the development of membranes with good hermodynamic and mechanically sustainable properties. In this case, inorganic membranes have great potential for producing hydrogen as an alternative fuel.

At the first stage of the research, the group of authors conducted an experimental study of electrolysis on a laboratory device designed to study the process of synthesis of new substances, pH correction, separation of amino acids, and separating the volume of inorganic compounds from organic solutions.

Figure 4 illustrates the electrodialysis rate of different concentrations of NaCl showing that the membrane is more effective when the NaCl concentration in solution varies from 10 g/l to 1 g/l. After this, based on the analysis of the results obtained, we will study the process of the Black Sea water desalination. Since the salinity of the Black Sea water is 15-16 m/l, so in terms of the effectiveness of the research, desalination was carried out until 5,77 g/l concentration. The process of desalination by electrolysis is shown in Table.

Table 1.

Time, min	*Current strength (amp)*	*Voltage (V)*	*Salt content (g/l)*	*Reduction of concentration*
0	2,15	30	5,77	—
15	1,2	30	2,94	49,1
30	0,4	30	0,457	84,5
45	0,1	30	0,052	88,8

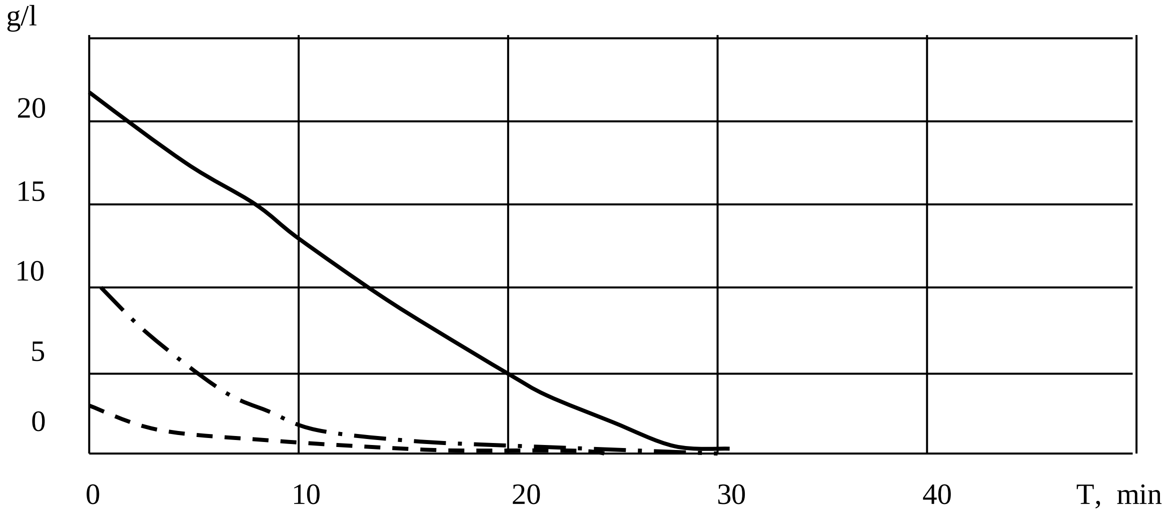

Figure 4. NaCl electrolysis rate: ——— NaCl 20,85 g/l.
–·–·– NaCl 9,75 g/l.
------ NaCl 2,09 g/l.

Based on the analysis of the research, we have identified the possibility of using membrane technologies in terms of desalination of the sea water, which allow us for using actively this method when studying the separation of hydrogen sukfide from the Black Sea water in a gaseous form. At this stage, the scheme is developed, the types of membrane are selected and the results of the research will be published in the near future.

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