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On the possibility of the utilization of hydrogen sulfide from the Black Sea

Abstract: Looking for alternative sources of energy to generate electricity has been a hot topic for society for a very long time. The need to replace current energy resources such as fuel, oil, and gas is increasing, and the replacement comes from energy obtained from the wind, sun, and sea waves. In many cases, valuable raw materials can be obtained in addition to energy production, while having a significant environmental effect simultaneously.

The shortage of energy and raw material resources in many countries stimulates the growth of interest in all potential sources of energy – solar, wind, wave, tidal – has lead to accelerating the demand for oil and gas, shale gas, as well as the expansion of the areas for the cultivation of technical crops for biofuels. Classical energy resources like oil, gas and coal are serious polluters of the

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natural environment. Especially harmful is the release of carbon dioxide and sulfur oxides during the exploitation of these resources.
A significant energy raw material potential of non-traditional resources lies in the waters and bottom of the Black Sea, which is a natural geobiotechnological reactor, capable of producing a variety of energy raw resources.
This paper discusses the use of hydrogen sulfide available in the Black Sea waters to produce energy and useful industrial products and proposes the respective. The technology also has an ecological effect in terms of the purification of the hydrogen sulfide pool. The paper also discusses some technologies for the separation of hydrogen sulfide to hydrogen and sulfur. An estimation of the heat value of hydrogen sulfide in the water of the Black Sea is also presented.

Keywords: hydrogen sulfide, Black Sea, H_2S utilization

Introduction

In recent decades, unconventional methods of energy production have been undergoing research and industrial experimentation (Etarski 1994; Demirbas 2006; Ushakov 2018; Kostov 2020). A large proportion of these studies has focused on the utilization of various gases that constitute emissions in industry, agriculture and households, as well as gasses from some natural sources (Baul et al. 2018; Krystev 2021; Lansche et al. 2017; Nyrkov et al. 2016). In addition to producing energy, in many cases, valuable raw materials can be obtained while simultaneously

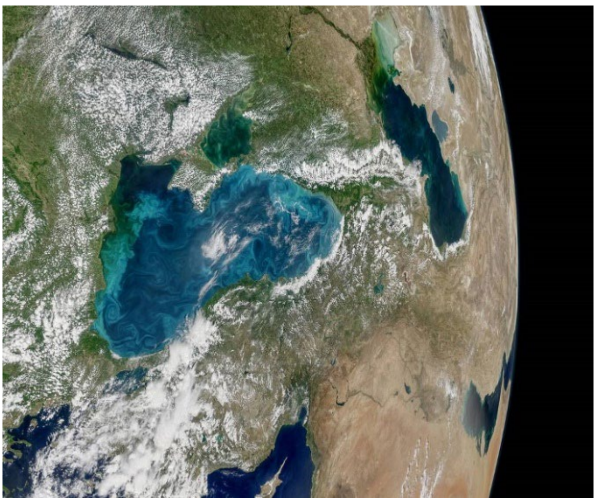


Fig. 1. Black Sea
Source: NASA 2021

Rys. 1. Morze Czarne

having a significant environmental effect. A typical example in this regard is the hydrogen sulfide (H_2S) released from various natural sources and, in particular, oil refineries (Ngene et al. 2016; Rubright et al. 2017; Myasnikova et al. 2019).

The significant energy and raw material potential of non-traditional resources lies both in the waters and at the bottom of the Black Sea (Fig. 1), which is a natural geo-biotechnological reactor, capable of producing a variety of energy and raw material resources (Budnik and Chernyi 2016; Nyrkov at al. 2016; Maksymova and Kostrytska 2018).

1. Hydrogen sulfide in the Black Sea

One of the hypotheses for the origin of the Black Sea is that 7500 years ago, it was the deepest lake on the earth. It is supposed to have been 100 m deeper than the present sea depth (Maksymova and Kostrytska 2018). With the end of the Glacial Era and the rise of the level of the world's oceans the Bosporus strait breached. A hundred thousand square meters of already cultivated lands were flooded. The hypothesis presumes that the formation of the Black Sea went along with mass mortality of life in the lake's fresh-water life. As a result of its decomposition, methane and hydrogen sulfide appeared as a by-product.

Today, the Black Sea is the largest H_2S field in the world. A characteristic feature of its structure is the presence of a deep-water H_2S layer at a depth of 130–200 m. This layer differs sharply from the upper surface layers in its properties. For these reasons, the phenomenon of upwelling is of particular importance for explaining the changes in the chemical and biogeochemical processes occurring in the water masses and at the bottom. This upwelling provokes the rise of waters from the H_2S layer, which are significantly more saline and rich in biogenic components (Fig. 2) (Demirbas 2006).

Figure 3 shows the gradual increment of the H_2S concentration from the surface of the Black Sea to the bottom (Dimitrov et al. 2003). In bottom sediments, H_2S contents range from 12––16 mg/l to 240 mg/l. The dissolved H_2S gas phase reaches 0.24 g/t at a depth of 300 m and 2.2 g/t at a depth of 2000 m. In seawater, H_2S is found not only in the dissolved gas phase but also as sulfides and hydrosulfides. The annual production of H_2S in the basin is 107–108 tons (Dimitrov et al. 2003).

The idea of using H_2S as an energy resource is attractive from an environmental point of view as it is linked to a waste-free technology.

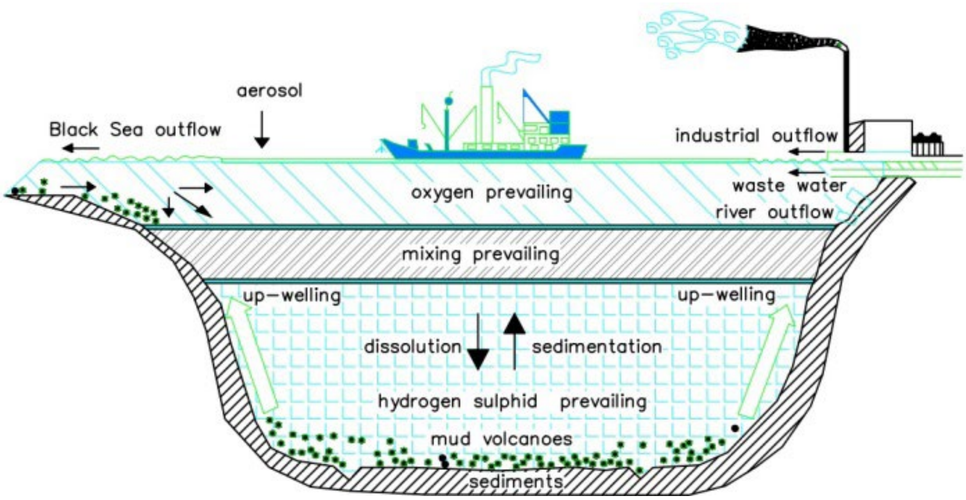


Fig. 2. The upwelling processes in the Black Sea
Source: generalized and systematized by the authors

Rys. 2. Procesy upwellingu w Morzu Czarnym

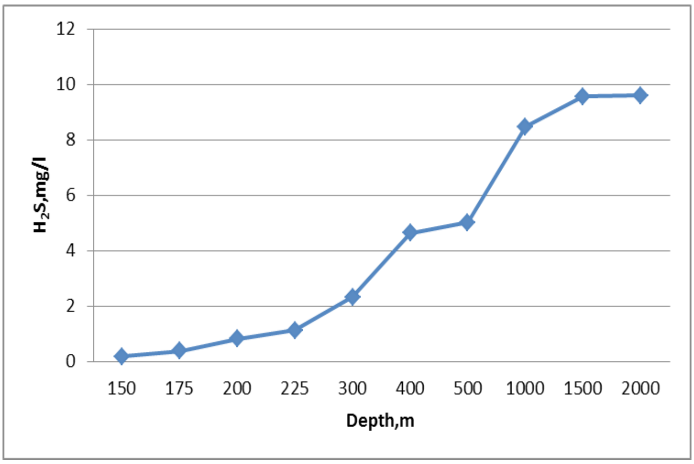


Fig. 3. Content of hydrogen sulfide in the Black Sea
Source: Dimitrov et al. 2003

Rys. 3. Zawartość siarkowodoru w Morzu Czarnym

2. Technological scheme for the utilization of the hydrogen sulfide in the Black Sea

Figures 4–7 present the technological scheme for the utilization of H_2S from the Black Sea waters.

Through pipeline 1, the water from the bottom of the Black Sea goes to vessel 2, where the water is separated from the hydrogen sulfide. The purified water from hydrogen sulfide returns to the Black Sea. Separation of hydrogen sulfide from water can be accomplished by any of the methods shown in Figure 8.

The separated hydrogen sulfide goes to vessel 3, where it is separated into hydrogen and sulfur by one of the following methods: thermal decomposition, thermal methods, Claus process or plasma dissociation. All these methods are described in details in (Velichkova et al. 2018). After the separation of hydrogen and sulfur, hydrogen would be used for energy production (vessel 5) and sulfur (vessel 6) for chemical or other industries.

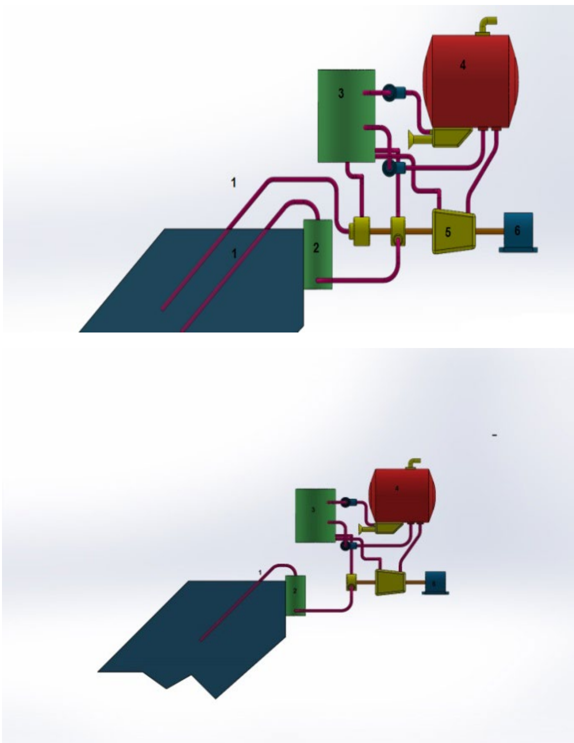


Fig. 4. Technological scheme
Source: generalized and systematized by the authors

Ryc. 4. Schemat technologiczny

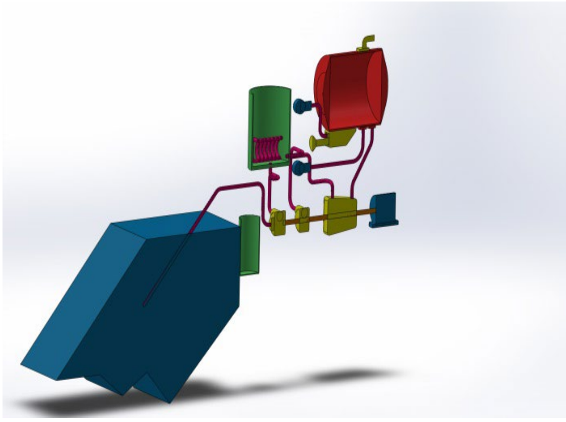


Fig. 5. Section of test-rig in front
Source: generalized and systematized by the authors

Rys. 5. Przekrój stanowiska badawczego z przodu

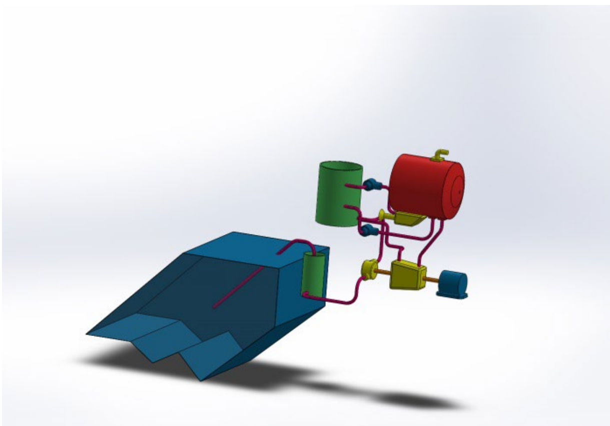


Fig. 6. Test-rig in front
Source: generalized and systematized by the authors

Rys. 6. Stanowisko badawcze z przodu

An important issue is the toxicity and corrosive behavior of hydrogen sulfide, which usually causes significant problems. Hydrogen sulfide is present in high concentrations in most natural gases and also in biogas and landfill gas.

Different methods for the removal of the hydrogen sulfide from Biogas installations are presented in Figure 8.

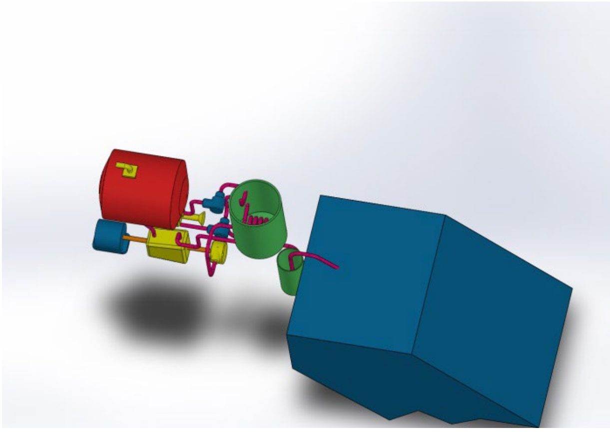


Fig. 7. Top of the test rig
Source: generalized and systematized by the authors

Rys. 7. Górna część stanowiska badawczego

3. Technological determination of the amount of sulfur in hydrogen sulfide and sulfuric acid

The section presents the determination of the amount of sulfur in H_2SO_4 and H_2S (Lide 2016).

The molecular weight of sulfuric acid (H_2SO_4) is 98.08.

$$s = \frac{m_s i_s}{\sum m_i i_i} = \frac{32 \cdot 1}{1 \cdot 2 + 32 \cdot 1 + 16.4} = \frac{32}{98} = 0.326531 \quad [\text{kg/kg}] \tag{1}$$

where:

m_s – the atomic weight of carbon ($m_s = 32$),

i – the number of atoms of the corresponding elements in the molecule.

For H_2S : $s = 0.94118$ [kg/kg]

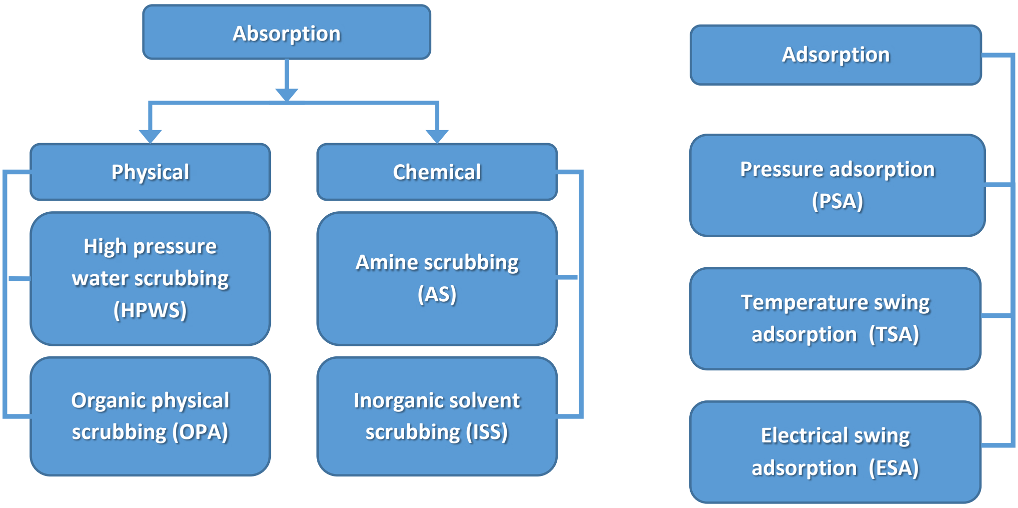
1 m^3 seawater contains 0.01925 [kg] sulfur on average.

In 1 [kg] H_2SO_4, there is 0.326531 kg sulfur.

From this comparison it can be calculated that 16.963 [m^3] hydrogen sulfide water is needed to obtain 1 [kg] H_2SO_4.

If the comparison is made with the same units, then from 1 [m^3] hydrosulphuric water, we can get $3.2 \cdot 10^{-5}$ [m^3] H_2SO_4 at an average concentration of H_2S in seawater of 12.5 [ml/l].

After the incineration of H_2S from SO_2, about 59 [g] H_2SO_4 is received. This quality is equivalent of 32 [cm^3] H_2SO_4.



H_2S Removal Methods	
Traditional methods	**Dry process**
	Liquid process
	Physical solvent
	Membrane process
Alternative methods	**In-Situ (Digester) Sulfid Abatement**
	Dietary Adjustment

Fig. 8. The removal process for H_2S
Source: generalized and systematized by the authors

Rys. 8. Proces usuwania H_2S

4. Calculation of the heat value of hydrogen sulfide

The calculation of the heat value of H_2S is as follows.
From the equation of Mendeleev:

$$H_p = 8100 \cdot c + 30000 \cdot h + 2600(s - 0) - 600(9h + w) \quad \text{[kcal/kg]} \tag{2}$$

$$c + h + o + w = 1 \quad [\text{kg}] \tag{3}$$

where:

c,h,o,w – are parts by the weight of carbon, hydrogen, oxygen and water in one kg fuel.

$$c = \frac{m_c i_c}{\sum m_i i_i}; h = \frac{m_h i_h}{\sum m_i i_i}; o = \frac{m_o i_o}{\sum m_i i_i}; o = \frac{m_w i_w}{\sum m_w i_w} \tag{4}$$

where:

m_c – the atomic weight of carbon (m_c =12),
m_h – the atomic weight of hydrogen (mh = 1),
m_o – the atomic weight of oxygen (m_o = 16),
i – the number of atoms of the corresponding elements in the molecule.

Typical data for H_2S
γ_{H_2O} = 1.54 kh/m^3 is the specific weight of the hydrogen sulfide

$$s = \frac{32 \cdot 1}{1 \cdot 2 + 32 \cdot 1} = 0.94118 \quad [\text{kg/kg}];$$

$$h = \frac{1 \cdot 2}{34} = 0.0588 \quad [\text{kg/kg}]$$

In 1 m^3, water from the Black Sea, there is an average of 12.5 [mL/L] H_2S (Varbanov et al. 2016).

$$H_{H_2S} = \frac{5981}{1540} = 3.884, \quad [\text{kcal/gr}] = 16.24 \quad [\text{MJ/kg}]$$

Therefore, 1 m^3 of water from the Black Sea would have a calorific value of:
$H_{B,S}$ = 16.24 · 19.25 = 312,62 [MJ/m^3]
with a mechanical equivalent of

$$L_M = 312.62 \cdot 427 = 133488.74 \quad \left[\frac{\text{kg.m}}{\text{m}^3}\right]$$

This obtained values shows that the installation can be very useful for use in practice.

Conclusion

A new idea for the utilization of hydrogen and sulfide from hydrogen sulfide in water in the Black Sea is presented. This technological scheme can be beneficial and helpful for the practice.

Besides, it would be more efficient for electricity production (using the hydrogen from hydrogen sulfide). The sulfur could be used in different industrial technologies.

From the calculations, it is clearly seen that the available hydrogen sulfide in the Black Sea has a high calorific value, i.e. the hydrogen sulfide available in the Black Sea can be used for the production of hydrogen or electricity, which will lead to a reduction in the carbon footprint.

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O możliwości wykorzystania siarkowodoru z Morza Czarnego

Streszczenie

Poszukiwanie alternatywnych źródeł energii do produkcji energii elektrycznej od dawna jest gorącym tematem w społeczeństwie. Konieczność zastąpienia obecnych źródeł energii, takich jak paliwo, ropa naftowa i gaz, jest coraz większa, a pochodzi ono z energii pozyskiwanej z wiatru, słońca i fal morskich. W wielu przypadkach, oprócz produkcji energii, można pozyskać cenne surowce, mając jednocześnie znaczący wpływ na środowisko.

Niedobór surowców energetycznych i surowcowych w wielu krajach stymuluje wzrost zainteresowania wszystkimi potencjalnymi źródłami energii – słońcem, wiatrem, falami, pływami – doprowadził do przyspieszenia popytu na ropę i gaz, gaz łupkowy, a także ekspansji powierzchni pod uprawę roślin technicznych na biopaliwa. Klasyczne źródła energii, takie jak ropa naftowa, gaz i węgiel, poważnie zanieczyszczają środowisko naturalne. Szczególnie szkodliwe jest wydzielanie się dwutlenku węgla i tlenków siarki podczas eksploatacji tych zasobów.

Znaczący potencjał surowcowy energii nietradycyjnych zasobów tkwi w wodach i dnie Morza Czarnego, które jest naturalnym reaktorem geobiotechnologicznym, zdolnym do produkcji różnorodnych surowców energetycznych.

W artykule omówiono wykorzystanie siarkowodoru dostępnego w wodach Morza Czarnego do produkcji energii i użytecznych produktów przemysłowych oraz zaproponowano odpowiednie rozwiązania. Technologia ma również efekt ekologiczny w zakresie oczyszczania basenu siarkowodoru. W artykule omówiono również niektóre technologie rozdziału siarkowodoru na wodór i siarkę. Przedstawiono również oszacowanie wartości opałowej siarkowodoru w wodach Morza Czarnego.

Słowa kluczowe: siarkowodór, Morze Czarne, wykorzystanie H_2S