An assessment of electrolytic hydrogen production from H$_2$S in Black Sea waters

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**Abstract**

In the deeper parts of the Black Sea basin, water is anoxic. Hydrogen sulfide (H$_2$S) occurs naturally, and its concentration is nearly constant, around 9.5 mg/L at 1500 m depth. Its high solubility, and the existing chemical environment facilitate its accumulation and containment in the seawater, and its extraction poses a challenge.

Possibility of hydrogen and sulfur production from H$_2$S contained in the waters of Black Sea is investigated conceptually. A multistage process is considered which involves extraction of seawater, adsorption of H$_2$S, electrochemical production of hydrogen and polysulfides; fresh water production by desalination of seawater and further hydrogen production from the resulting salty solution through chlorine–alkaline electrolysis. Some consideration is included regarding the economic and environmental aspects of the process.

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**1. Introduction**

Black Sea is the largest anoxic basin in the world, where almost 90% of the seawater is anaerobic. Anoxic conditions prevail underneath the thin oxygenated surface water layer which is separated by an oxygen–hydrogen sulfide (H$_2$S) interface which exists at nearly 150 m below the surface. In this region, H$_2$S is produced through a microbial sulfur cycle. Its concentration grows with depth, and reaches a maximum of 10 mg/L at 2000 m [1–6]. The total sulfur budget is believed to be $4.6 \times 10^9$ ton [1].

Hydrogen sulfide is a poisonous, flammable and corrosive gas. Seawater infused with H$_2$S can be considered as a non-ideal solution. Here, the solubility of H$_2$S is expected to vary with temperature, pH, salinity and pressure. In Black Sea, the natural pH level is around 8, and extraction of H$_2$S may be possible by lowering the pH to nearly 4 and elevating the temperature [3].

Feasible methods are needed for remediation of wastewaters or gases with low concentrations of H$_2$S. There are many examples of factories and utilities with dump lakes around the world which can be remedied.

The potential for hydrogen and sulfur production from H$_2$S in Black Sea and industrial wastewaters using renewable energy sources, especially solar and wind, is significant. Hydrogen sulfide can be converted to hydrogen and sulfides...
with much less energy than that is required for splitting water (H₂O). Various methods are available [6] for hydrogen production from H₂S that are at different stages of development.

In the present work, preliminary investigations have been carried out regarding adsorption and electrolysis of H₂S. As a result of these studies, the amount of a specific type of activated carbon (in grams) required for adsorption of H₂S from 1 L of seawater in 1 h was determined. Simultaneously, studies on electrolyzer performance were carried out and operation conditions were specified. Rest of the studies were dedicated to process and plant design, energy requirement, and economics with the aim of estimating capital investment, plant efficiency, and product cost.

2. Hydrogen from Black Sea concept

Following a conceptual study involving solar hydrogen production by thermal decomposition of H₂S from Black Sea [5], a process for electrolysis of H₂S using renewable energy is considered presently.

The process design can be divided into two main stages in view of the available techniques for production of hydrogen, sulfides (sulfur) and sweet water: (i) Extraction of HS⁻/CO₂ from seawater followed by electrochemical production of H₂ and polysulfides; and (ii) Desalination of seawater for producing fresh water and concentrated salt solution.

The process in consideration is shown in Fig. 1a, which is also suitable for the treatment of industrial wastewaters (Fig. 1b).

Variation of H₂S concentration in Black Sea waters is presented in Table 1 [1,2]. It can be seen that after 1500 m depth, the figures for H₂S and HS⁻ are almost constant.

The process (Fig. 1), consists of an adsorbent column (1), into which seawater from 1500 m depth, containing H₂S and NaCl is pumped. In this column H₂S is separated from seawater by selective adsorbent materials i.e., activated carbon. By treating the adsorbent with NaOH, a solution containing HS⁻ + NaOH is obtained, which is sent to an electrolyzer (2), where hydrogen (H₂) and polysulfides (S) are produced. An evaporator is needed with the purpose of increasing electrolyte concentration in the feed stream to the electrolyzer. Electrolysis is executed in an alkaline solution. Seawater with reduced H₂S can be released back to the sea, or it can be further processed via membrane separation technology producing fresh water and concentrated salt solution which can be further utilized in chlorine–alkaline electrolysis to produce additional hydrogen provided that NaCl concentration is around 320–360 g/L. The concentrated salt solution can also be utilized by the PVC industry in case there is one in the vicinity (Presently, PVC factories in the region obtain the salty solution from underground crystal salt deposits by injection of water hundreds of meters below ground, and pumping the solution to the surface and transporting it via pipeline for about 20 km). These factories may buy the polysulfides as well in order to produce special polymers and resins.

Adsorption and electrolysis modules constitute the main unit of the process in consideration. Electricity for electrolysis can be obtained by renewable energy (solar and wind).

In Black Sea, the main unit can be installed either on the shore (Fig. 2a) or on the sea floor (in an old military submarine, for example, as in Fig. 2b). Hydrogen produced can be sent to the shore by pipeline. In some cases where the deep waters are far from the shore (Bulgaria, Romania, Ukraine) an oil platform may be used for supplying electricity to the main unit and for collecting hydrogen.

2.1. H₂S adsorption/desorption

Adsorption of H₂S by activated carbons has been studied extensively [7–16]. The system under consideration involves a gas extraction process in which the Black Sea (or industrial waste) water is passed through a bed of activated carbon particles as hydrogen sulfide selective adsorbent. As the compressed fluid is passed through this bed, hydrogen sulfide is adsorbed from the fluid, and afterwards it is recovered with NaOH solution. After hydrogen sulfide removal the resulting product is water with salts. This byproduct can be further processed in order to obtain sweet water.

Performance of carbons in terms of hydrogen sulfide adsorption depends on surface chemistry, large surface area and porosity of carbon [9], and its pH level [11]. Natural pH level of Black Sea water is around 8. By lowering the pH to 4, extraction of H₂S can be possible [3]. Unmodified activated
carbons (pH levels in the range 3.8–4.5) can be considered for this purpose [11]. Removal of H₂S (adsorbate) from carbon can be carried out by treating with NaOH and transferring into solution. Concentration of the resulting HS⁻/CO₃⁻ solution is increased in an evaporator, before electrolysis.

Activated carbons and carbon fibers have been used for many years, quite successfully, for regenerative adsorptive/desorptive removal of impurities from exhaust gas and wastewater streams [7–9]. The mechanism of removal of H₂S (from a fluid stream) by activated carbon includes acid–base neutralization [11]. Based on the detailed study of surface chemistry it has been suggested that hydrogen sulfide breakthrough capacity is governed by the local pH within the pore system. This local pH depends on the pore sizes and the location of acidic groups [10–12]. A critical value in carbon surface acidity is known to exist, which when exceeded results in a negligible hydrogen sulfide breakthrough capacity [9]. To ensure effective removal of H₂S, pH values higher than 5 are required. Low pH in the local pore environment suppresses H₂S dissociation and reduces the removal capacity, while high pH results in high concentration of hydrogen sulfide ion [9]. Since the basal plane of the graphite material is considered hydrophobic, carbon structures have to be activated. This treatment makes the carbon surface more hydrophilic and increases wettability compared to the raw carbon [13].

Activation process and the nature of organic precursors have the main influence on the surface area and porosity of carbons [9]. Activated carbons are prepared by physical and chemical processes. Chemical activation involves treatment with alkali or acids. In physical activation, carbonization of a carbonaceous precursor takes place, and the resulting char is activated by CO₂ or steam [16].

Chemical activation with phosphoric acid for example, may lead to activated carbons with highly developed porosity and consequently with advanced adsorption properties [13].

Further development of surface area and porosity can be achieved through partial gasification with CO₂ [13].

Granular activated carbons with a wide range of pore size distribution and with high adsorption capacity have been produced through combined activation — physical activation with carbon dioxide of previously phosphoric acid activated materials. In such applications, porosity developed by physical (CO₂) activation is a function of porosity developed by chemical activation (H₃PO₄).

Using this approach, activated carbons, ranging from microporous to mesoporous structure can be prepared [13].

Activation is necessary for increasing the storage capacity of the adsorbant. The adsorption mechanism is based on the Van der Waals forces established between the H₂S molecule and the active centers from the internal (real) surface of the carbonic layer [9]. Therefore, large surface area and microporosity are especially important features in unmodified activated carbons [9].

Method of activation, surface chemistry and porosity may lead to significant differences in the performance of unmodified activated carbons as H₂S adsorbants [10,12]. Combined effect of presence of pores large enough for accommodating surface functional groups and small enough to accommodate water is important [10,12]. Heterogeneous carbon (containing micro- and mesopores) which has surface functionality performs better than neutral, microporous carbons with high surface area [10]. Mechanism of H₂S adsorption by unmodified carbons involves dissociation of H₂S into hydrogen sulfide ions (HS⁻) [9] in the water film adsorbed at the carbon surface. The mechanism in caustic impregnated carbons involves a process catalyzed by caustic [9].

The major reaction is [15,16]:

H₂S + AOH → AHS + H₂O

or,

H₂S(aq) + NaOH(s) → NaHS(aq) + C + H₂O

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Table 1 – Hydrogen sulfide content in Black Sea waters [1,2].

<table>
<thead>
<tr>
<th>Depth, m</th>
<th>ΣH₂S (mol/L)</th>
<th>H₂S, gas (mol/L) × 10⁻⁵</th>
<th>HS⁻ (mol/L) × 10⁻⁵</th>
<th>%, ΣH₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>9.53</td>
<td>28</td>
<td>4.1</td>
<td>24</td>
</tr>
<tr>
<td>1750</td>
<td>9.83</td>
<td>29</td>
<td>4.1</td>
<td>25</td>
</tr>
<tr>
<td>2000</td>
<td>10.19</td>
<td>30</td>
<td>4.0</td>
<td>25</td>
</tr>
</tbody>
</table>

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Fig. 2 – Possibilities for main unit installation in Black Sea.
Impregnation of carbon with caustic materials leads to an increase in H$_2$S breakthrough capacities. In impregnated activated carbon systems, specific surface area, micropore area, and micropore volumes become reduced [15]. When NaOH is introduced in significant amount onto the surface, pore blocking is likely, leading to a decrease in the active surface area [14].

Different kinds of impregnates were introduced for improving the H$_2$S removal capacity by activated carbons. Bagreev and Bandosz [14] studied the effect of NaOH on adsorption of H$_2$S, using four different kinds of carbons, with different amounts of impregnated NaOH. They found that impregnation of NaOH significantly improved H$_2$S removal capacity. However, when more than 10% of NaOH was introduced, pore blocking was likely. Again, they found that the H$_2$S removal capacities were dominated by the presence of NaOH, and were not sensitive to surface areas and pore structures of these activated carbons. Other reports on NaOH [15,16] impregnation also showed significant improvement of the H$_2$S removal capacity. It is believed that the presence of alkaline chemicals facilitates the dissociation of H$_2$S on carbon surfaces [15,16].

Adsorption mechanism of H$_2$S by NaOH impregnated activated carbons is a process catalyzed by NaOH [9]. It is possible to specify an activated carbon and alkaline solution blend to obtain the best H$_2$S adsorption on alkaline-activated carbon [16]. If the adsorption equivalent is 1 for H$_2$S (mol H$_2$S/mol NaOH), 0.0425 g H$_2$S would be adsorbed per gram of carbon when the optimum NaOH concentration is 50 mg/g of carbon [16].

In view of regeneration of exhausted carbons, up to 60% irreversible capacity loss is possible following the first adsorption run [9] (due to deposition of elemental sulfur in carbon micropores and strong adsorption of sulfuric acid leading to low pH). However, after the first regeneration using water washing, some capacity remains, which is maintained at a more or less constant level through the new few adsorption/regeneration cycles [9]. In regenerating using heat treatment, around 30% of initial H$_2$S adsorption capacity may be retained through heating at 573 K [9].

Preliminary studies have been conducted in ICIT Romania using industrial carbon (AD3 IPMP Buzau). The carbon is an untreated market product, and its adsorption capacity is determined as 0.0021 g H$_2$S/g of activated carbon. Based on this capacity, calculations for Black Sea water with an average H$_2$S concentration of 8 mg/L, indicate that 3.8 kg activated carbon is needed to adsorb H$_2$S from 1 L of seawater in 1 h. It is necessary to have two reactors working in sequence, one adsorbing and the other recovering with NaOH.

When H$_2$S concentration in the inlet stream is low, capacities of unmodified carbons can be comparable to those of caustic impregnated carbon [11,14]. Performance of Romanian unmodified activated carbon (0.0021 g H$_2$S/g C) is comparable to values reported in literature [11,14], but lower than optimized caustic impregnated carbon [16].

2.2. Electrolysis

Direct electrolysis of hydrogen sulfide in alkaline solutions has been investigated by several authors [17–20]. The cathodic process, hydrogen evolution in alkaline solution, is simple and well known. A membrane is necessary to separate the cathodic compartment from polysulfide ions produced at the anode. Sulfur ions can be electrochemically oxidized to elementary sulfur, polysulfides and sulfides, depending on the electrolytic conditions, i.e. overpotential, pH and temperature. The process has been studied over the years mostly in order to purify waste or natural gases from H$_2$S. According to Anani et al. [21] the best conditions are: $T \approx 89$ °C, $pH = 13–14$ and low overpotential $E < 0.6$ V. In previous studies [22] parameters such as catalyst performance, influence of CO$_2$, concentration of sulfur ions and sulfur species, hydrogen evolution, and cell parameters have been investigated.

Through long-term tests of 500 h, stable cell voltage of 1.0 V was obtained at current density of 300 mA/cm$^2$, using 2 M NaOH and 8 M NaHS at 80 °C; with Raney-nickel cathode, perovskite anode and Nafion membrane [22].

Raney-nickel, graphite, platinized carbon, CoS and perovskites (La$_{0.2}$Sr$_{0.8}$MnO$_3$) were tested as catalysts. The electrodes with perovskite and CoS catalysts were highly stable and their performance was close to that of Pt. Approximately 500 h of long-term tests were performed without changes in their characteristics. Current density values up to 1.0 A/cm$^2$ were obtained at anode potential of 0.6 V (RHE) and Tafel slope of about 30 mV/decade.

The results indicate that the presence of carbon dioxide leads to a decrease in the current density at a given potential. It is probably due to the well-known process of carbonization of NaOH, which lowers the conductivity of the solution. Addition of supporting electrolyte (NaCl) compensates this effect. This is important in the case of Black Sea waters where NaCl is abundant. The other possible components in the seawater are MgCl, and various metal ions. Theoretically, only transition metals like Fe, Cd, Co, etc. can be oxidized at the potential of H$^+$ (0.003–0.097 V [23]); however, due to their very low concentrations and reaction kinetics, their influence should be negligible in this case.

Electrolyzer performance improves with concentration of HS$^–$. At high concentrations of sulfur ions (10 M NaHS) a high current density of 1.0 A/cm$^2$ at anode potential of 0.6 V (RHE) can be reached.

In proportion with the time length of electrolysis of HS$^–$ in NaOH and NaCl solution the average length of polysulfide chain increases. When most of the HS$^–$ (about 70%) are converted to low polysulfides, S$_n$S$_{n–1}$, polysulfides with higher chain length are also obtained. At this stage, the process goes on at lower current density and constant potential. This requires the use of flow type electrolyzer. Close to the inlet of it, where the concentration of HS$^–$ is high, the current density will be about 1.0 A/cm$^2$. Along the length of the electrolyzer the concentration of HS$^–$ and the current density will decrease. At the end of electrolysis, where the concentration of HS$^–$ is almost zero and the polysulfide chain length is high, S$_n$S$^{n–1}$; the current density is 150 mA/cm$^2$.

During hydrogen evolution, the only problem appears to be the possible migration of polysulfides to the cathode department, which can be prevented using a membrane-like Nafion. The tests have shown stable cathode potential of 150 mV (RHE) at electron density of 750 mA/cm$^2$. Measurements of the amount of hydrogen evolved indicate cathodic efficiency values close to 100%.
3. Water pipeline

Extraction of anoxic seawater from the depths will have the advantage of high pressures exerted by the water column. At 2000 m, nearly 19.6 MPa pressure would be available, for example, decreasing the energy requirement for pumping considerably.

On the other hand, for the release of processed water a deep discharge line would be more suitable, however costly. Preliminary information regarding the water pipeline is given in a previous article [5].

In this respect, submerged operation may be ecologically less interfering, despite the complexity that might be involved with the transportation of the products to the surface. This mode of operation could be possible by building a vertically mobile plant capable of surfacing in order to unload.

4. Ecological concerns

Black Sea is the world’s largest and most stable anoxic marine basin. Natural water conditions as well as the endemic1 biological communities are unique and extraordinary, and they deserve preservation [24–26].

Vertical density structure of the sea contains waters with relatively low salinity (18%) in the surface layer below which salinity increases up to 22% in the deeper water column. A permanent pycnocline2 with significant density gradients divides these two distinct water bodies. The main pycnocline is located between constant density levels 14.5 and 16.5 and it is separated into the upper and lower sections at density level 15.5 [2]. The onset of sulfide is generally accepted to be located at the depth which coincides with the density level 16.2. The average location of oxycline varies between the density levels (14.4–14.6) and (15.6−15.9). Between the lower boundary of the oxycline and onset of sulfide, which correspond to density levels of (15.6−15.9) and 16.2, the sub-oxic layer is located [2].

Vertical mixing is inhibited by stratification which promotes anoxic conditions below approximately 100–150 m. Spatial structure of the basin can be sensitive to anthropogenic disturbances. As indicated by the results of studies carried out through the past decades, a decrease in the inventory of oxygen in the upper layer, an increase in the inventory of sulfide and nutrients in the anoxic water column, and variations in the thickness of the sub-oxic zone are in progress, and these changes can be attributed to an increase in the flux of sinking particulate organic matter [2].

Ecological concerns vary regarding the two distinct water bodies in Black Sea, the anoxic basin and the oxygenated shelf.

4.1. Deep-water section of the Black Sea

The anoxic deeper water column in the basin, besides being enriched in H2S, contains other biogeochemically reduced species such as NH4, PO4, CH4; and trace elements (dissolved sulfide, manganese, iron, copper, and zinc).

At the interface between oxygen and H2S, due to variations in conditions related to redox and solubility of bacterial activity, large changes may occur in the state of ions.

Contamination of the uppermost photosynthetic layer of Black Sea by its deep waters may result in anthropogenic upwelling3 and intensified eutrophication.4

Microbial sulfate reduction (SR), is a dominant process of organic carbon mineralization in deep anoxic waters of the Black Sea. Hydrogen sulfide, as a terminal product of this bacterial respiration, accumulates in the water environment as well as in the seabed sediments. Biosegregation, i.e. organic carbon fluxes from a zone of photosynthesis into the H2S-zone is the leading factor which determines SR-activity in the Black Sea. At the present time, anthropogenic eutrophication of the upper layer has increased the flux of carbon into the deep-sea anoxic water body and consequently, the rate of hydrogen sulfide production. Therefore, reducing the amount of H2S in the Black Sea by the employment of environmentally friendly technologies could improve the ecological conditions and the security in the region.

4.2. Periphery of the Black Sea H2S-zone

Near the shelf, vertical fluctuations of the H2S-interface up to 35 m in height have been detected within water column depths of 130–165 m. These fluctuations can cover a horizontal distance more than 1 km from the sea floor. Thus, a belt-like zone with high variability of oxic/anoxic conditions exists in the near-bottom layer, located over the Black Sea shelf-break. It is most important for the recently discovered deep-water communities of the Black Sea meobenthic5 fauna. Intensified anthropogenic activity near the shelf-break, significant enough to alter the ratios of O2/H2S, Mn4+/Mn2+ and NO3−/NH4+ may lead to unfavorable chemical and ecological consequences.

Evaluation of the environmental impact should be carried out for each process, by: (i) monitoring of key integral parameters of the Black Sea redox system, (ii) study of activity and dynamics of anaerobic microorganisms when deep-sea waters are brought to the surface and released back into the Sea; and (iii) experimental investigations of reactivation of the dormant stages of oxybionts,6 which are taken from the Black Sea H2S-zone and also study of influence on planktonic and benthos7 organisms by oxygenated deep-sea waters.

5. Considerations on energy consumption and economic aspects

The process for hydrogen from H2S in Black Sea, is quite energy intensive. A brief financial evaluation is carried out based on the process equipment [27] and the simplified

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1 Habitually prevalent.
2 Density slope.
3 Rising to the surface.
4 Promotion of nutrition.
5 Relating to flora and fauna of bottom of the sea.
6 Living in oxygen.
7 Flora and fauna of bottom of the sea.
economic approach developed for cost estimation [28]. Assumptions used in the evaluation are given in Table 2.

Preliminary studies indicate that basically two stages of the process in consideration consume most of the energy supply: transportation of seawater by pipeline (44%) and harvesting and concentration of H2S through adsorption/desorption and evaporator units (55%). Shares of these stages in installed equipment cost are 95% and 2.3%. Energy consumption and equipment cost shares estimated for electrolysis are 2.5% and 1.8% respectively (Table 2). Overall energy efficiency of the process, calculated as the ratio of energy value of hydrogen produced to total energy consumption is around 1.95%.

Assuming that capital charges and energy consumption constitute the main components of annual expenses, production costs for hydrogen and sulfur are estimated as 23.14 Euro/m³ and 15.425 Euro/kg respectively. If the products are sold at prices given in Table 2, the production costs would be reduced slightly, to 20.14 Euro/m³ for hydrogen, and to 15.1 Euro/kg for sulfur.

On the other hand, activated carbon has to be replenished since its adsorptive capacity is diminished, despite regeneration. If a fresh batch is supplied every week, production costs for hydrogen and sulfur may increase to 30.6 Euro/m³ and 20.4 Euro/kg. Based on annual energy cost only, production costs for hydrogen and sulfur from H2S in Black Sea could be 14.6 Euro/m³ and 9.73 Euro/kg.

However, if the process is used on-site for hydrogen and sulfur production from industrial wastewaters containing H2S at low concentrations, installed equipment cost is 20 times less. In this application, 97.5% of the energy consumption takes place in H2S generation stage; rest is used in electrolysis mainly. Nearly 47% of installed equipment cost is allocated for H2S generation, and 38% for electrolysis; rest is mainly for storage tanks. Overall energy efficiency is nearly 3.5%. Manufacturing costs of hydrogen and sulfur from H2S in industrial wastewaters using this process are respectively 8–16 €/m³ H2 and 5.46–10.74 €/kg S.

A straightforward economic approach could be the determination of market value of hydrogen and sulfur produced annually. Using the EU target price for hydrogen from renewable energy, 3.00 €/m³, and the market price for sulfur, 350 €/ton; value of 8000 m³/y hydrogen and 12 ton sulfur would amount to 24,000 €/y and 4200 €/y, 28,200 €/y in total which corresponds to 24% of the cost of energy requirement of the plant which uses H2S from Black Sea. When industrial wastewaters are used as H2S source, this ratio is higher, 43%.

These figures are well above the market prices for hydrogen and sulfur. However keeping in mind that the profit here is not a commercial one, they can be interpreted as the cost figures for saving Black Sea and the way of life around it.

6. Conclusions

A technically feasible and ecologically agreeable technology for consumption of H2S in the Black Sea waters and production of hydrogen, sulfides (sulfur) and sweet water using renewable energy sources like solar and wind can be developed.

With the intention of using electricity at relatively lower prices and being closer to the industrial sector where the products from the electrolytic hydrogen production process can be used, west coast of Black Sea, where water depth is less, is chosen for conceptual plant location. Consequently, calculations were based on conditions at 1500 m maximum water depth. Each country in Black Sea region may carry out studies for site selection as in the study for hydrogen production by solar thermolysis of H2S in Black Sea water [5].

Since displacement of large volumes of seawater from the depths is required by the technology in consideration, thorough ecological surveillance and follow-up of the impact of such industrial activities are important. Primarily, extraction of H2S-rich water and its discharge after processing should be carried out at levels deeper than 200 m, outside the oxygenated surface layer. Due to ecological concerns as such, in situ operation may be preferred.

Solar thermolysis [5] and electrolysis using electricity by renewables may be equally challenging and expensive mainly due to low concentration of H2S even in deep waters. In electrolysis, if electricity by renewable energy is obtained via grid system, continuous operation can be possible. On the other hand, solar thermolysis could be limited by the intermittent nature of in situ solar radiation.

Energy equivalence, in terms of commercial fuels, of the H2S content of Black Sea has been estimated [29]. Limited evaluations are available on the economics of hydrogen from H2S [30,31] and from H2S in Black Sea [27]. Further investigations are needed for economic assessment of hydrogen production from H2S in Black Sea. For the process plant in consideration, operating cost, which constitutes most of the production cost will heavily depend on the commercial price of renewable electricity produced by solar and/or wind technology and supplied to the grid. Targeted market price for hydrogen 0.20 Euro/m³, proposed by the European Union (EU) appears to be quite unlikely using this technology. The EU target price for hydrogen from renewable energy, 3.00 Euro/m³ [32] could be a more realistic benchmark presently.

However, considering the relatively early state of development of the process in consideration and its economy of scale, cost of hydrogen from H2S in Black Sea may gradually shift closer to that of hydrogen from solar water electrolysis in

<table>
<thead>
<tr>
<th>Table 2 — Economic assumptions.</th>
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<tbody>
<tr>
<td>Annual operation time</td>
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<tr>
<td>Annual production of hydrogen</td>
</tr>
<tr>
<td>Annual production of sulfur</td>
</tr>
<tr>
<td>Annual energy (electricity)</td>
</tr>
<tr>
<td>Installed equipment cost</td>
</tr>
<tr>
<td>Capital charge rate</td>
</tr>
<tr>
<td>Price of electricity (renewable) from the grid</td>
</tr>
<tr>
<td>Price of activated carbon</td>
</tr>
<tr>
<td>Selling price (EU) of hydrogen</td>
</tr>
<tr>
<td>Selling price of sulfur</td>
</tr>
</tbody>
</table>

a Hydrogen production from H2S in Black Sea.
b Hydrogen production from H2S in industrial wastewaters.
c Selling price of hydrogen produced using renewable energy.
the long-term. This shift may take place sooner for cost of on-site hydrogen from H₂S in industrial wastewaters.

Under present circumstances, hydrogen production does not have a commercial motive, but it is rather an initiative which can be financed as a municipal service for the remediation of Black Sea from H₂S; and the cost involved can be interpreted as the cost of protecting the priceless oxygenated surface waters and the sustainability of economy in the coastal region.

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