HYDROGEN PRODUCTION FROM H_2S IN BLACK SEA AND INDUSTRIAL WATERS USING GREEN ENERGY

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ABSTRACT:

The aim of this work is to investigate the potential of H_2S in Black Sea and industrial waste waters for production of hydrogen and sulphides using green energy sources like sun and wind. H_2S can be converted to hydrogen and sulphides with much less energy than splitting H_2O (water). The thermodynamic potential of H_2S oxidation is $E_{H2S}=0.17$ V compared with $E_{H2O}=1.23$ V for water splitting.

Different processes for H_2S conversion are evaluated: (i) extraction of H_2S from sea (or industrial) waters by absorbents and electrochemical production of hydrogen and polysulphides; (ii) additional desalination of the Sea water for producing fresh water and salty solution mainly. The salty solution is processed in chlorine – alkaline electrolysis producing the main amount of H_2. Various applications of the main unit (H_2S separation and Electrolysis) for industrial waste or sea waters are considered. Assumptions are made for the environmental impact of each process in particular.

KEY WORDS: Black Sea, Hydrogen Sulphide, Industrial waste waters

INTRODUCTION

Black Sea is an elliptical basin with an area of 423.000 km^2. More than 100 million people live around its coast. Black Sea is unique because 90% of the sea water is anaerobic. The anoxic conditions exist in the deepest parts of the basin where H_2S is believed to be produced by sulphur reducing bacteria at an approximate rate of 10 000 tons per day.

It poses a serious threat since it keeps reducing the life in the Black Sea.

An oxygen–hydrogen sulphide interface is established at 150 – 200 m below the surface after which H_2S concentration starts increasing regularly until 1000 m, and finally

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reaches a nearly constant value of 9.5 mg/l around 1500 m depth [1, 2].

Lowering H_2S concentration is an ecological and engineering challenge and feasible methods are not developed up to now. Such technology can be used for cleaning waste waters or gases from industrial sources with low concentrations of H_2S. It can be applied to improve the ecological conditions and for hydrogen production in many places including the Black Sea region.

Black Sea countries do not have their own energy sources like natural gas and oil, and they are becoming more and more dependant on imported fuels.

New energy technologies, based on Hydrogen as an energy carrier, are emerging. European countries, including Black Sea ones, are among the most interested in applying these technologies in order to decrease their dependence on energy import and environmental pollution.

Cheep and abundant production and storage of Hydrogen are the major issues in the future Hydrogen Energy Economy.

1. PROPOSED PROCESS DESIGN

The proposed process design is a summary of the ideas presented by some of the authors in their previous papers [3, 4]. Based on prominent techniques for hydrogen, sulphides (sulphur) and sweet water production the process design can be divided into two stages:

(i) Extraction of HS^- from sea (industrial) water on absorbents followed by electrochemical processes for H_2 and polysulphides production; and (ii) Membrane desalination of sea water for producing fresh water and concentrated salt solution (CSS).

H_2S concentrations in Black Sea waters [2] and the proposed process design are presented in Table 1 and Figure 1.

Table 1 shows that at 1500 m depth total H_2S concentration is C_{H2S}=9.53 mg.l^{-1},or 28 mol.l.10^{-5}, where SH^- ions content is C_{SH-} = 24 mol.l.10^{-5}, and H_2S gas is Cg=4.1 mol.l.10^{-5}. The proposed process design (Figure 1), consist of absorbent column (1), where sea water from 1500 m depth, containing H_2S and NaCl is pumped into.

In this column H_2S is separated from sea water by selective absorbent materials. By regenerating the absorbent with NaOH a solution containing HS^- + NaOH is released. Resulting solution of NaSH +NaOH is sent to an Electrolyzer (2). NaSH +NaOH solution is converted by electrolysis to H_2 and polysulphides, both commercial products. In addition to electrolysis a photochemical processes can be considered.

The salty water without H_2S can be released into the Sea, if there is no threat to the ecological balance.

The developed process for electrolysis of H_2S can be applied for cleaning the waste H_2S from any industrial source.

A second stage can be to further process the sea water without H_2S by use of membrane separation technology.

As a result, fresh (sweet) water and concentrated salt solution (CSS) will be produced.

Table 1
H_2S content in Black Sea waters

Depth, m	∑ H_2S		H_2S, gas	HS^-	
	mg/l	mol/l.10^{-5}	mol/l.10^{-5}	mol/l.10^{-5}	%, ∑ H_2S
1500	9.53	28	4.1	24	86
1750	9.83	29	4.1	25	86
2000	10.19	30	4.0	25	83

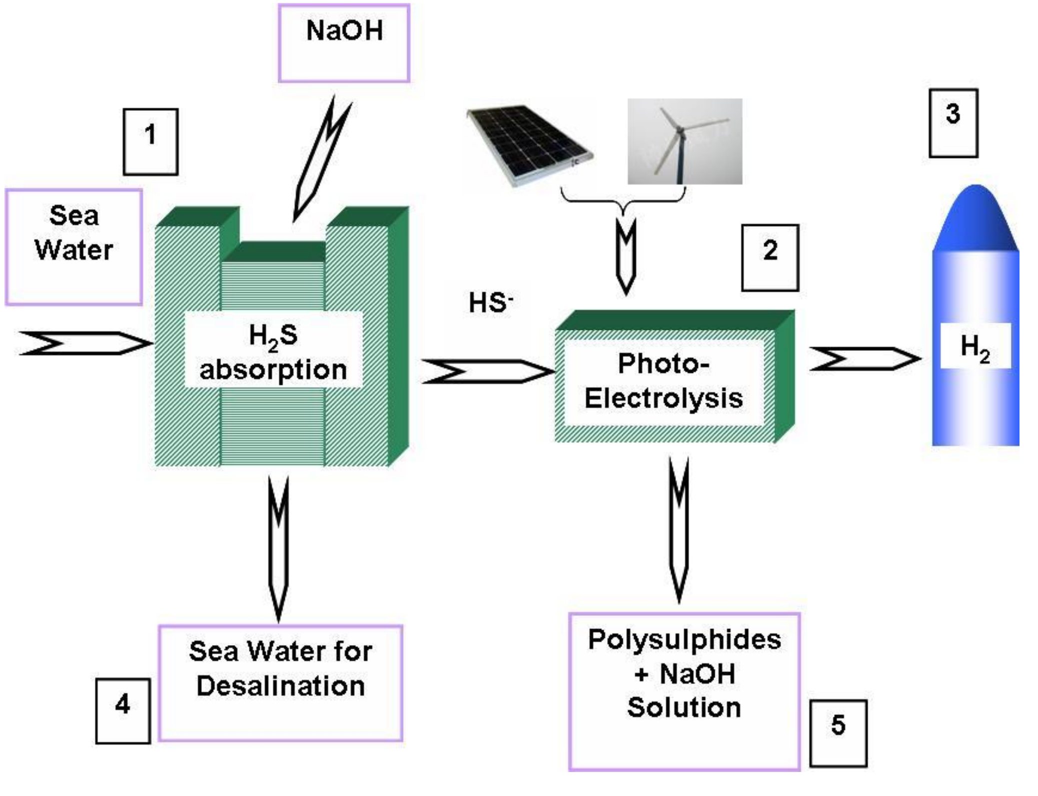

Fig. 1: Flowchart of the process in consideration

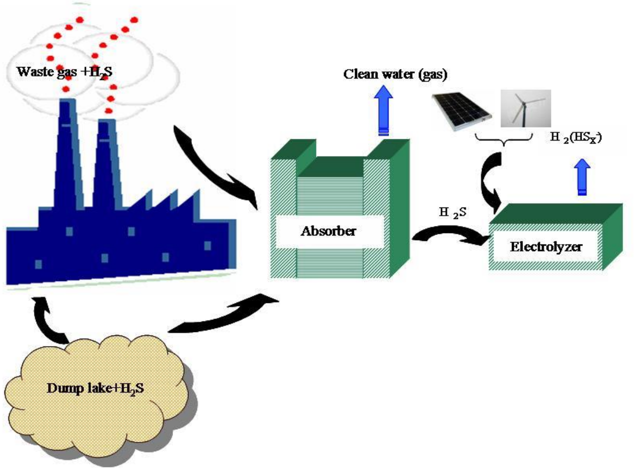

Figure 2 Application of the Absorption/Electrolyzer Unit for cleaning of industrial waste waters and gases

The concentration of NaCl should be 320 – 360 g.l^{-1} in order to be used further in chlorine – alkaline electrolysis. This is the most developed electrochemical industrial process which produces H_2, NaOH and Cl. Now PVC factories provide the salty solution from underground crystal salt deposits. They inject water 100’s of meters below the surface, pump the solution to the surface and transport it by pipeline about 20 kilometers. This is the case in PVC factories in Devnja, around Varna, Bulgaria and Oltchim, Romania. These factories may buy the polysulphides as well, in order to produce special polymers and resins.

Absorption and electrolysis units constitute the core of the process in consideration. Combined they can be used for remediation of the water from H_2S and hydrogen production. Such a technology can be used for cleaning waste waters or gases from industrial sources. H_2S at low concentrations constitutes an ecological and engineering challenge and feasible methods are not developped so far for dealing with it.

The following diagrams present the possibilities for application of this process.

Figure 2 shows schematically the main unit (H_2S separation and Electrolysis) for cleaning industrial waste waters and gases. The electricity for electrolysis is obtained by renewable energy (Sun and Wind). There are many examples factories and utilities with dump lakes around the world.

Figure 3 shows a possible process for extracting Black Sea water from 1500 m depth. Water is pumped to the shore where the main unit (H_2S separation and Electrolysis) is installed. Electricity is generated by the Solar and Wind generators. The sea water, cleaned from H_2S is released back into the sea.

Another option that can be considered is shown in Figure 4. In this case the main unit (H_2S separation and Electrolysis) is installed at the bottom of the Black Sea. Electricity is provided by the Solar and Wind generators installed on the shore. Hydrogen produced is sent to the shore by pipeline.

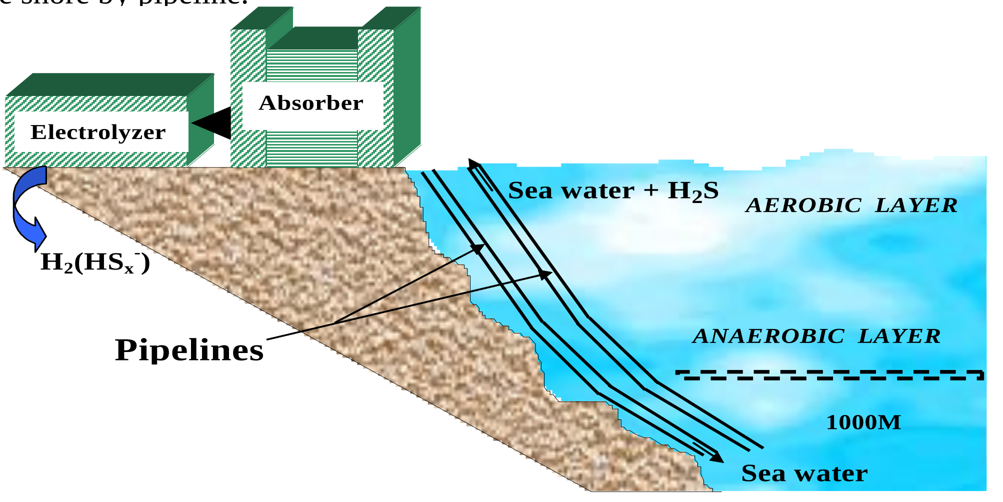

Figure 3 Application of the Absorption/Electrolyzer Unit on the shore of the Black Sea

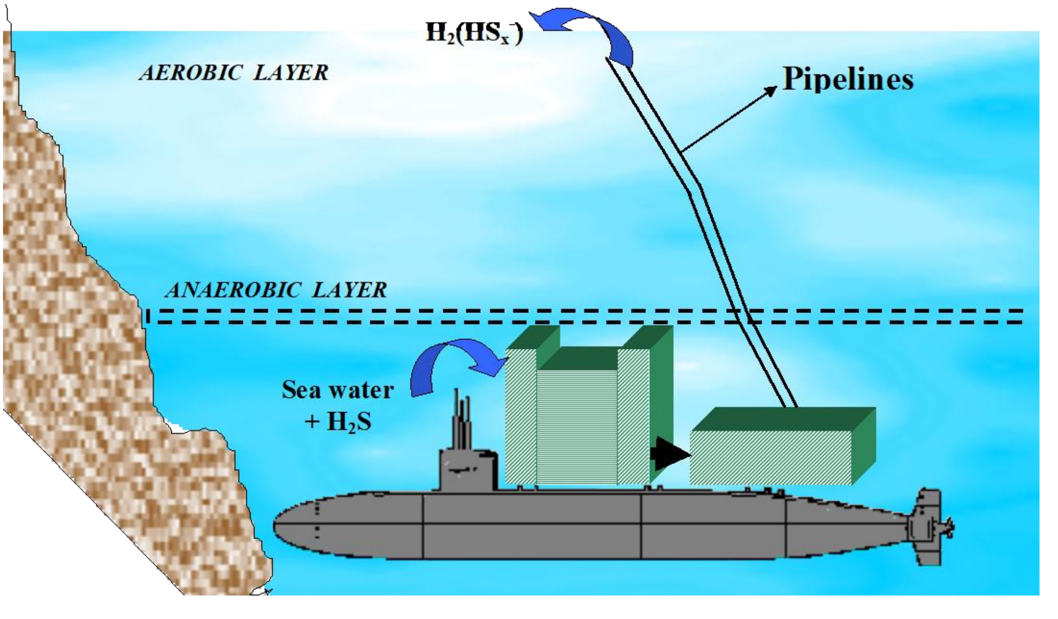

Figure 4 Application of the Absorption/Electrolyzer Unit on the bottom of the Black Sea

The H_2S separation and Electrolysis units may even be installed in an old military submarine. 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 (H_2S separation and Electrolysis) installed at the bottom and for collecting Hydrogen.

2. DESCRIPTION OF THE MAIN PROCESSES

2.1. H_2S Adsorption/Desorption

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 [5-7].

Based on the detailed study of surface chemistry it has been suggested that hydrogen sulfide breakthrough capacity is governed by local pH within the pore system. This local pH depends on the pore sizes and the location of acidic groups [8-10]. Since the basal plane of the graphite material is considered hydrophobic, carbon nanostructures have to be activated with CO_2, steam or other polar molecules. This treatment makes the carbon surface more hydrophilic and increases wettability compared to the raw fibers [11].

In this respect, prior to utilization as H_2S adsorbant, the carbon nanostructures have to be activated with CO_2, steam or other polar molecules. The activation is necessary for increasing the storage capacity of the adsorbant by enlarging the pores. The adsorbtion mechanism is based on the Wan der Vaals forces established between H_2S molecule and active centers from the internal (real) surface of the carbonic layer.

Different kinds of impregnates were introduced for improving H_2S removal capacity by activated carbons. Bagreev et al. [12] studied the effect of NaOH on adsorption of H_2S, using four different kinds of carbons, with different amounts of impregnated NaOH. They found that impregnation of NaOH significantly improved H_2S removal capacity. However, when more than 10% of NaOH was introduced, it likely resulted in pore blocking. Again, they found the H_2S 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 [13, 14] impregnation also showed significant improvement of the H_2S removal capacity. It is believed that presence of alkaline chemicals facilitates the dissociation of H_2S on carbon surfaces.

The innovative system that we propose in this paper is to build up a process in which the Black Sea or waste water is passed through a bed of activated carbon adsorbent particles comprising hydrogen sulfide selective adsorbent. As the compressed fluid is passed through this bed, hydrogen sulfide is adsorbed from the fluid. The resulting product, containing adsorbed hydrogen sulfide, is then desorbed under special conditions in order to recover the hydrogen sulfide that is used as the hydrogen source. The resulting product after hydrogen sulfide removal is water with salts. This byproduct can be then processed in order to obtain sweet water.

2.2. Electrolysis

Direct electrolysis of hydrogen sulfide in alkaline solutions has been investigated by many authors [15-18]. The cathodic process – hydrogen evolution in alkaline solution is simple and well known. Membrane, is necessary to separate the cathodic compartment from polysulfide ions produced at the anode. Sulfur ions can be electrochemically oxidized to elementary surlfur, 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 puriufy waste or natural gasses from H_2S. According to Anani et al [19] the best conditions are: $t^o=89^oC$; pH = 13-14 and low overpotential E<0.6 V. In our own studies [20] the following parameters have been investigated:

catalyst performance: Raney-nickel, graphite, platinized carbon, CoS and perovskites ($La_{0.79}Sr_{0.20}Mn_40_3$) were tested. The electrodes with perovskite and CoS catalysts show performance close to Pt and are very stable with time – 500 hrs long term tests without changes in their characteristics. The best results were: up to i=1.0 A.cm^{-2} at anode potential E_{an}= 0.6 V (RHE) and Tafel slope of about 30 mV decade^{-1}.

influence of carbon dioxide presence: the results show that presence of carbon dioxide decreases the current density at the same potential. It is probably due to well-known process of carbonatization of NaOH, which decreases 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.

influence of concentration of sulfur ions: performance increase with concentration of SH- ions. At high concentrations sulfur ions (10 M NaSH) a high current density of i=1.0 A.cm-2 at E_{an}= 0.6 V (RHE) can be reached.

influence of concentration of different sulfur species: with the time of electrolysis of SH^- ions in NaOH and NaCl solution the average length of polysulfide chain increases. When most of the SH- ions (about 70 %) are converted to low polysulfides, S_2S^-, polysulfides with higher chain length are obtained. At this stage 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 SH^- ions is high the current density will be about i=1.0 A. cm-2. Along the length of the electrolyzer the concentration of SH^- ions will decrease, as well as the current density. At the end of electrolysis, where the concentration of SH^- ions is almost zero and the polysulfide chain length is high S_6S^- , the current density is i=150 mA.cm^{-2}.

hydrogen evolution: in case of hydrogen evolution the only problem is possible passing of polysulfides to cathode department, which can be prevented by use of membrane like Nafion. The tests have shown stable cathode performance of E_c=150 mV(RHE) at i=750 mA.cm^{-2}. The measurements of the amount of the evolved hydrogen show cathodic efficiency close to 100 %.

cell parameters: long term test of 500 hrs at following conditions: NaOH=2M; NaSH=8M; T=80oC; cathode from Raney-nickel; anode is $La_{0.79}Sr_{0.20}Mn_4 0_3$; Nafion membrane; shows stable cell voltage of Ecell=1.0 V at i=300 $mA.cm^{-2}$.

2. 3. Environment protection

The Black Sea is unique, being the world largest H_2S marine basin. Vertical density structure of this sea containes low-salinity waters in the surface layer (~18 $^0/_{00}$) and more saline environment in the deeper water column (~22 $^0/_{00}$). These two distinct water bodies are divided by the permanent pycnocline with significant density gradients. Such a sharp stratification inhibits vertical water mixing and it is the main reason of the anoxic conditions below around 150 m. This spatial structure of a basin can be sensitive to disturbances which may possibly result from future anthropogenic activities. Unique Black Sea natural water conditions as well as the endemic biological communities are extraordinary [21,22] and hence must be protected in any case. Since the above suggested technologies intend to move big volumes of deep Black Sea water, the ecological control for these industrial activities should be detailed and comprehensive.

The ecological concerns differ for the two distinct water bodies in the Black Sea.

Deep-water section of the Black Sea: its lower zone is highly enriched not only in H_2S - a strong respiratory toxin, but also by many another bio-geochemically reduced compounds, such as NH_4, PO_4, CH_4, Mn etc. Therefore, in case of contamination of the uppermost, photosynthetic layer of the Black Sea by its deep waters it can produce an effect of anthropogenic upwelling and strong intensification of already observable eutrophication.

However, on the other hand, one dominant process of organic carbon mineralization in deep anoxic waters of the Black Sea is microbial sulfate reduction (SR). Hydrogen sulphide as a terminal product of this bacterial respiration accumulates in the water environment as well as in the seabed sediments. Biosedimentation, i.e. organic carbon fluxes from a zone of photosynthesis into the H_2S-zone is the leading factor which determines SR-activity in the Black Sea. At the present time anthropogenic eutrophication of the upper layer of the Black Sea are to be observed. It has increased the flux of $C_{org.}$ into its deep-sea anoxic water body and also it should quite definitely increase the rate of hydrogen sulphide production. Therefore, reducing the amount of H_2S in the Black Sea by environmentally friendly technologies could improve the ecological conditions in the Black Sea and therefore the security in the region.

periphery of the Black Sea H_2S-zone: earlier, near the shelf, tsunami-like but oft-recurring vertical fluctuations of H_2S-interface within the water-column depths of 130-165 m, i.e. up to 35 meters in height have been detected. As result, these fluctuations can cover a horizontal distance more than 1 km from the sea floor. Thus, a belt-like zone of high variability of oxic/anoxic conditions exists in the near-bottom layer, located over the Black Sea shelf-break. Above all, it is most important for benthic organisms because of recent detections of deep-water communities of the Black Sea meobenthic fauna. Heavy technological activity near the shelf-break can exert influence on O_2/H_2S, Mn^{+4}/Mn^{+2}, NO_3^-/NH_4^+ ratios with ecological and chemical consequences.

Evaluation of the environmental impact of their application should be carried out for each process, in particular: (i) monitoring of key integral parameters of the Black Sea redox system – Eh, pH, S^{2-}, O_2, C_{org}. etc.; (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 oxibionts, which are taken from the Black Sea H_2S-zone and also study of influence on planktonic and benthos organisms by oxygenated deep-sea waters.

2. 4. Water pipeline

Extraction of anoxic seawater from the depths will have the advantage of high pressures erected 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, the release of processed water batch to the sea at the surface into the oxygenated layer would be hazardous environmentally and a deep discharge would be more suitable, however costly.

Preliminary information regarding the water pipeline is given in a recent article by Baykara et al. [4].

CONCLUSIONS

A commercially feasible and ecologically compatible technology for reduction of H_2S in the Black Sea waters and production of hydrogen, sulphides (sulphur) and sweet water using green energy sources like sun and wind can be developed.

Using green energy for production of sweet water, hydrogen and sulphides (sulphur) from H_2S in Black Sea waters is going to deliver great economical and ecological benefits to the people living in the area.

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