Possibilities of Production and Storage of Hydrogen in the Black Sea

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ABSTRACT:

Black Sea, a highly-isolated inland sea, is the largest anoxic zone in the world. Since the hydrogen sulphide zone was discovered in early 19th century in the Black Sea, it has been adopted that there is no life in the depths of the Black Sea and there are only bacteria live in the hydrogen sulphide layer. High content of organic matter, with maximum processes of bacterial sulfate reduction is the major source of this hydrogen sulphide zone.

Hydrogen sulphide is one of the most poisonous gases in the world but it has great economic value to obtain hydrogen via dissociated into hydrogen and sulphure. Thus the Black Sea is not only has a serious environmental contamination but also has potential source of hydrogen energy, if a decomposition process can be developed.

In this study, the sources of hydrogen sulphide, environmental impact of hydrogen sulphide in the Black Sea, the available techniques of hydrogen production from hydrogen sulphide and the possibilities of hydrogen storage by the natural sources in the Black Sea have been investigated.

KEYWORDS : *Hydrogen Sulphide, Hydrogen Energy, Hydrogen Storage, Black Sea*

1. INTRODUCTION

The Black Sea, a highly-isolated inland sea, has a transition layer, called suboxic zone that has simultaneously low concentration of oxygen and low concentration of hydrogen-sulfide. Hydrogen sulphide layer appears in the Black Sea, mainly because it is highly isolated from the open ocean, when oxygen consumption due to the input of decomposable organic matter sinking from the upper euphotic zone or added by rivers flowing into the sea exceeds the oxygen supply to deep waters. Hydrogen-sulphide in the Black Sea, whose source is the process of anaerobic decomposition of organic matter of sulfate-reducing bacteria, is one of the world's most poisonous and is a possible energy source today.

The structure of the study is as follows: the next section is about the organic matter composition in the Black Sea. Following this, the formation and balance of Hydrogen-sulfide is explained and the available techniques of hydrogen production are presented. Then, After producing of H_2S, possibilities of the storage of hydrogen in coastal line caves in the Black Sea are proposed. Finally, a proposal is made for production of Hydrogen from Hydrogen-sulfate to be extracted from the waters of Black Sea and storage by the natural sources of the Black Sea.

2. ORGANIC MATTER CONCENTRATIONS IN THE BLACK SEA

During the last 40 years, the Black Sea environment has a serious degradation from the waterborne waste from European countries. Black Sea is a highly-isolated inland sea and 17 European countries drain into it. Due to this reason and natural sources, waters of the Black Sea are anoxic. [1]

In the Black Sea, dissolved and particulate organic matter concentrations decrease with depth. In the upper layers, they are controlled by the photosynthetic input and respiration process and by the supply from rivers. The riverine sources carry both dissolved and suspended organic matter of various origins.

The large natural river supply of nitrogen and phosphorus compounds, are the main nutrients triggering eutrophication, has always made the Black Sea very fertile. But, now, serious degradation of them is the main reason of ecological problems in the Black Sea. The majority of nutrients, 53% of the nitrogen and 66% of the phosphorus, discharged into the Black Sea come from the Danube River. 115,000 tons of oil enters the Black Sea each year, with %48 of it coming from the Danube. Approximately total discharge of the Danube is 203 km^3 each year. The nutrients introduced into the Danube originate from agriculture(chemical or organic fertilizer, Irrigation…), Metropolitan and Industrial Wastes (Petroleum chemicals, Lumber, Wood-pulp Industry..) and domestic sources. But the Danube is not the only pollution source. The other major rivers flowing into the Black Sea and their total discharges are: Dnieper-Ukraine (54 km^3/yr^{-1}), Dniester-Moldova (9,3 km^3/yr^{-1}), Don-Russia (28 km^3/yr^{-1}), Kuban-Russia (13 km^3/yr^{-1}), Kızılırmak, Sakarya, Yeşilırmak-Turkey (41 km^3/yr^{-1}). [1]

Table 1. Total Nitrogen and Phosphorus Pollutant Loads in the Black Sea (GEF, Report 1996)

	Total Nitrogen (TN) Pollutant Loads				**Total Phosphorus (TN) Pollutant Loads**			
Sources	**Domestic (t/y)**	**Industrial (t/y)**	**Riverine (t/y)**	***SubTotal* (t/y)**	**Domestic (t/y)**	**Industrial (t/y)**	**Riverine (t/y)**	***SubTotal* (t/y)**
Bulgaria	2.482	71.000	1.985	75.467	693	0	432	1.125
Georgia	1.577	7	1	1.585	435	0	0	435
Romania	877	44.394	102	45.373	260	254	14	528
Russia	414	1	13.076	13.491	502	2	533	1.037
Turkey	5.430	578	32.000	38.008	2.188	69	3.600	5.857
Ukraine	9.514	30.954	2.362	42.830	2.577	1.699	362	4.638
National	**20.294**	**146.934**	**49.526**	**216.754**	**6.655**	**2.024**	**4.941**	**13.620**
Danube				345.660				25.440
Dnieper				11.180				3.970
Dniester				22.750				980
Don				7.048				3.386
Sea of Azov				43.900				3.100
International				**430.538**				**36.876**
Total				***647.292***				***50.496***

3. H_2S IN THE BLACK SEA

The Black Sea has a large anoxic zone (90% of the sea water is anaerobic). It has a hydrogen sulphide rich layer, is about 50 m thick, between anaerobic and aerobic water lies at a depth of approximately 200 m along the axis of the Black Sea. Hydrogen sulphide concentration increases steadily from the anoxic interface with depth to a concentration of 300 µM at 1000 m, below which it increases slightly to about 400 µM at 1900 m. At a depth of more than 1900 m, the concentration of hydrogen sulphide is practically constant. Hydrogen Sulphide and Dissolved oxygen concentrations are shown in Figure 1. [2]

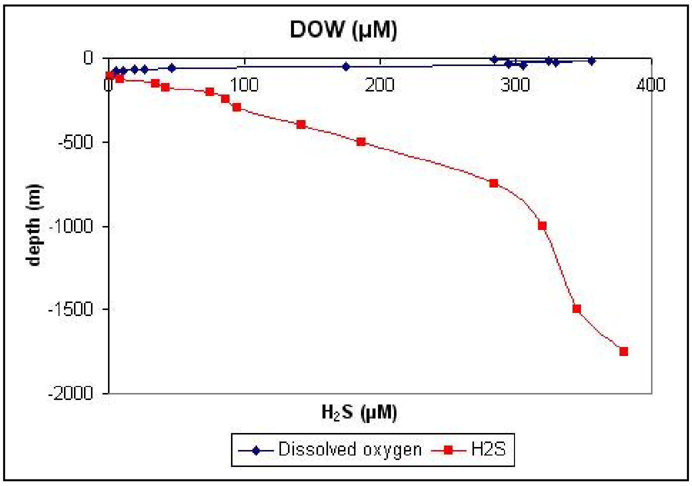

Figure 1. Hydrogen Sulphide and Dissolved oxygen concentrations in the Black Sea obtained by using the data from March – April 1995 cruise of R/V Bilim.

Total sulphide production in the sediments of the sea is estimated as 10,000,000 kg/day^{-1} and the hydrogen sulphide content in the Black Sea increases because the sea has not yet reached a steady state, meaning that it continues to change. [3]

This hydrogen sulphide zone in the Black Sea originates from bacterially mediated dissimilatory sulfate reduction. Other important sources of hydrogen sulfide are the geological sources.

3.1 Sulfate-Reducing Bacteria

The bacteria utilize, first, the free dissolved oxygen in order to decompose the sinking organic matter. When the dissolved oxygen concentration is below 2-4 mg/L, combined forms of oxygen are used as electron sinks by the bacteria to oxidate. The first groups of compounds that supply the combined oxygen are nitrates (NO_3^-) and nitrites (NO_2). Metal oxides, sulfates (SO_4^-), carbon dioxide (CO_2) and even water itself are used by bacteria as electron sinks in parallel to the decrease in redox potential of the water mass. [4]

Sulfate-reducing bacteria, one of the oldest known life forms on the planet, are the anaerobic bacteria that utilize sulfate as an oxygen source. The reduction of the sulfate is accomplished by sulfate - reducing bacteria;

$$2\ CH_2O + (SO_4)^{-2} \longrightarrow 2\ (HCO_3)^- + H_2S$$

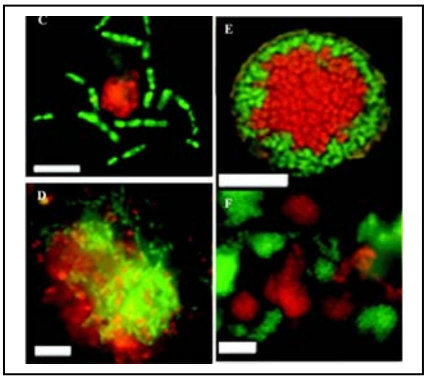

Figure 2. Electron micrograph of Sulfate-Reducing Bacteria

Sulfate reducing bacteria thrive and dominate the bacterial population, when the free oxygen concentration decreases below 1 mg/L.

The most abundant bacterial population in the Black Sea belongs to the Sulfate - reducing bacteria Desulfosarcina/Desulfococcus group. When oxygen consumption due to the input of decomposable organic matter sinking from the upper euphotic zone or added by rivers flowing into the sea exceeds the oxygen supply to deep waters, these bacteria thrive their population and utilize sulfate as an oxygen source. As a result, the concentration of H_2S increases, reaching to 8-10 mg/l to depths of 1,500 m. [5]

3.2 The Geological Sources

Fractures and mud volcanoes, as well as the destroyed gas-hydrate deposits, which contain the solid phase of H_2S. At the same time, from earth shells through the cracks in the sea ground and with hydrothermal waters.

As a chemically active component H_2S, is liberated from the volcanoes and is absorbed by the iron coming from the land and is fixed on the sea bottom in the form of undissolved iron sulfides. An interesting fact is that together with iron sulfides, gas hydrates were also formed in the sediments from the glacial period. In the near future, it is quite possible to prove that hydrogen sulfide, liberating from the throats of mud volcanoes on the bottom. [2]

4. PRODUCTION OF HYDROGEN FROM H_2S

Hydrogen could be produced from H_2S by using various different decomposition methods. These main methods are thermal, electrochemical, photochemical, the plasma and thermochemical,

4.1 Thermal

Thermal decomposition is the most direct process to dissociate H_2S into H_2 and S. When the temperature of the superheated steam is raised to 1200 K, the H_2S start dissociating into H_2 and S.The process needs no intermediary chemicals. Catalysis could be useful to increase the conversion level. [6]

4.2 Photochemical

Photochemical reactions use photocatalysts that absorb ultra-violet light from the solar spectrum to power chemical reaction. But this method is not effective since using UV light is very expensive to produce Hydrogen from H_2S. [7]

4.3 Electrochemical

In this method an electrolysis cell is used to produce hydrogen and sulfur from hydrogen sulphide by letting the direct electric current pass between the two electrodes of the cell like water electrolysis method. This method has three different techniques: Direct, indirect, high temperature.

Direct electrolysis can be performed in acids or alkaline media. [8]

Indirect electrolysis methods use a chemical oxidant to oxidize H_2S in acidic or basic media. [9]

In high temperature electrolysis, hot H_2S flows past the cathode, where hydrogen is evolved. The sulphide ion moves through a molten salt electrolyte to the cathode. [10]

4.4 Plasma

The plasma process uses microwave plasma chemistry to dissociate H_2S into H_2 and S. Back reaction of the products to H_2S is minimized by in situ cyclonic separation and a rapid quench of the products. Furthermore, experiments with water and carbon dioxide concentrations typical of acid-gas streams from refinery operations and natural gas production have demonstrated that these components are compatible with the proposed process. A preliminary economic evaluation indicates that the plasma-chemical process will be substantially cheaper to operate than the conventional sulfur recovery technology and that the sulfur emissions will also be lower. [11], [12], [13]

4.5 Thermochemical

Most of the hydrogen sulfide produced in the catalytic hydrodesulphurization of fossil fuels is processed in a Clauss process, producing sulfur and low-valued steam but doesn't produce any hydrogen. But for a long time, it has been known that H_2S can be converted to H_2 and elemental sulfur by thermal decomposition of H_2S at high temperatures (900-1100 K). H_2S can be catalytically decomposed to hydrogen and sulfur and the catalyst preparation, operating conditions, catalyst type have a significant effect on the amount of hydrogen produced and on the economics of the process. The stoichiometric equation of the thermal decomposition reaction is [14]

$$2H_2S \rightleftharpoons 2H_2 + S_2 \qquad \Delta H = 50 \text{ kcal/mol (Activation energy)}$$

5. STORAGE OF HYDROGEN

Secondary energy source which is called "energy transporter" has obtained transformation from firstly energy sources around world. Hydrogen is an energy transporter of 21st century's.

Hydrogen has a different security character with its physical specialty from other fuels. If there is any leakage in area, hydrogen increases the atmosphere and disperses because of its lowly density. In this case, a good ventilation provide safety for animate.

Hydrogen can be produced from water, fossil fuels, biomass and geothermal energy. Produced hydrogen can be transport to far away with hydrogen pipe lines.

Hydrogen can be storage as gas or liquid in tanks. It can be storage in physically carbon nannotubes or chemically as hydrur.

As gas hydrogen generally store in underground cave where is over natural gas in it. With this way leakage problem can be solved great extend in the storage area. France has successfully applications on hydrogen storage. Hydrogen may also store in tanks as gas. But when hydrogen stores as gas, tanks have been heavier because of high pressure. Hydrogen has four times more volume from oil. To reduce of volume hydrogen can be store as liquid in tanks. In this case tanks need huge area for deposit. With this reason, gas storage has advantage in caves. Hydrogen has been stored as gas 1330 m. deep from ground in a cave in Kiel city (Germany) since 1971. This storage way is more cost but it looks more safety from others. Every year %1-3 of hydrogen may be loose by leakage as water or water vapour. Selection of cave is also important in this situation. [15]

5.1 Storage of Hydrogen as Gas in Caves

Cave is naturally formed opening beneath the surface of the Earth, generally formed by dissolution of carbonate bedrock. Caves may also form by erosion of coastal bedrock, partial melting of glaciers, or solidification of lava into hollow tubes. The inception of cave development in carbonate rocks (karstic) begins if water can move through the bedrock and commence dissolution. Similarly inception may include physical and chemical dissolution as well as by the carbonic acid dissolution that dominates later cave growth. Initial water movement can be along primary pores in the rock along relatively thin noncarbonated beds within the succession, or along incipient or open fissures. [16], [17]


Figure 3. Caves

Cave is a one of the karstic constitution. The others are panor, polye, sink, doline and cenote. These are different type gaps in karstic area. For example polye can be continue several kilometers along, covered with fairly flat alluvium and with steep walls.

Karstic structure has different kind gaps. With this reason before the hydrogen gas storage cave's structure has to be known well to pretend the leakage of gas.

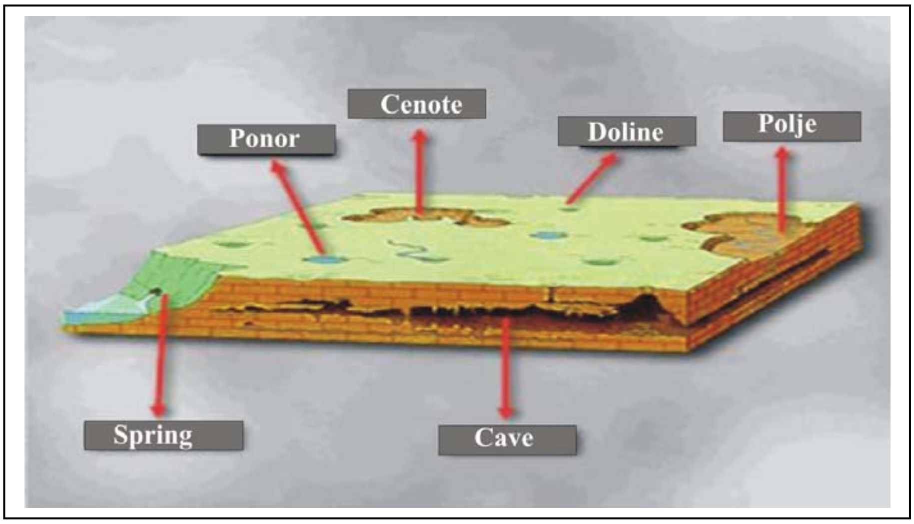

Figure 4. A Cave In Karstic Area

5.2 Hydrogen Storage in the Black Sea-Turkey

Black Sea has been north of Turkey (Figure).

Figure 5. Black Sea

Black Sea region in Turkey has too many caves. After producing of H_2S from Black Sea, storage of hydrogen might be done in coastal line caves as gas. Especially Zonguldak, Sinop, Kastamonu cities have huge caves(Figure). In this study some of caves has selected for hydrogen storage.

Figure 6. Zonguldak, Sinop, Kastamonu cities have been caves

Selected Caves in Zonguldak

Gökgöl Cave, Kızılelma Cave, İnağzı Cave, Cumaayanı Cave. [18]

Kızıl elma Cav es might be suitable for hydrogen storage. It is second longer cave in Turkey. The deepest point is 3200 m. There is a funnel in this dept. If the all gaps find in caves it may be useful for storage. We offer that this area must be investigate.

Gökgöl Cave and Cumaayanı Caves have been full of water in winter and spring, so it doesn't useful for storage of hydrogen.

Selected Cave in Sinop

İnaltı Cave

This cave has 700 m. long. It is muddy after 400 m. Travertine has been occurred in cave. İnaltı Cave also can be investigated for storage of hydrogen.

Selected Cave in Kastamonu

Ilgarini (Ilvarini) Cave

This cave is the fourth biggest cave around the world. It also might be investigate for storage of hydrogen.

6. CONCLUSION

Natural accumulation of organic matter and Hydrogen-sulfide possess a great environmental threat for the Black Sea. Hydrogen sulphide is one of the most poisonous gases but at the same time such a good source of hydrogen and sulphur, if a decomposition process can be developed. The decomposition process can provide reduction of environmental pollution and produce hydrogen to use in the future energy technology, "Hydrogen Energy".

The Black Sea has an advantage to store the hydrogen, due to their natural geology. After producing of H_2S from the Black Sea, storage of hydrogen might be done in coastal line caves as gas.

We propose that the Hydrogen-sulfide in the Black Sea could be used as a source of Hydrogen by separating Hydrogen-sulfide via any of the available methods after it has been extracted from the sea water and the possibilities of hydrogen storage by the natural sources in the Black Sea could be a good way to solve the hydrogen storage problem.

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