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SOLUTIONS FOR REDUCING DISSOLVED HYDROGEN SULPHIDE IN THE BLACK SEA BY ELECTROCHEMICAL OXIDATION

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Anaerobic disintegration of organic matter has a particular phenomenon in the Black Sea because of the set up of deposits of hydrogen sulphide - H_2S having big concentration. The reason of these deposits is the absence of upward streams at depth over 100 meters. In Black Sea there are under oxic layer placed between rough. 50 and.200 meters from witch begin anoxic layer. If the equilibrium in Black Sea is not guarded, it's possible an ecological disaster. The first signals will be observed in surface waters, than, if the equilibrium is further on disturbed the depth sulphides and the hydrogen sulphide can developed to inflammable phases and even explosive. This paper presents some solutions to reduce the hydrogen sulphide from Black Sea making accent on electrochemical method.

Key words: dissolved hydrogen sulphide, electrochemical oxidation, Black Sea, in-situ process, H_2S fuel cell.

1. Introduction

The Black Sea is an ellipsoidal basin having a surface of approximate 423.000 km^2, a medium depth of 1.263 m and a water volume of approximate 534.000 km^3.

In the Black Sea the nitrogen and phosphorus compounds are the principals nutrients responsible for eutrophise process and the source of the highest ecological problems. Majority of the nutrients, 53% nitrogen and 66% with phosphorus, in Black Sea come in from the Danube river. Approximate 115.000 tons oil come in the Black Sea, with 48% proceeded from the Danube river. Nutrients from Danube proceed from the agriculture, waste products and industrial products. The same type of the effluents proceeds from the Dnieper (Ucraina), Dniester (Moldova), Kizilirmak, Sakarya, Yeşilirmak (Turkey). Anoxic layer in the Black Sea is in majority (90% from the depth waters). In these areas there is a high contents of organic matter and a bacteriological process, important sources the hydrogen sulphide. The concentration of the hydrogen sulphide rise with the depth being 8 ml/litre at 1000 m, with a little rise to 8,5 ml/litre at 2000

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m. At the sea bottom the concentration may be of 13,5 ml/l. Total deposits of the hydrogen sulphide in the Black Sea is approximate to 8587 billion tons of H_2S.

In these conditions we can establish that at depth over 60 m in Black Sea there is no live, and because of hydrogen sulphide toxicity there is a permanent diminution of the alive organisms (over 3000 dolphins die every year).

2. The potential of hydrogen from the Black Sea

The studies certainly demonstrated that the huge H_2S quantities from the depths of the sea are very dangerous, forming toxic deposits for the marine flora and fauna. Hydrogen sulphide seawaters depleting of, was subject of many studies and projects and implies important high costs. Clean exploiting of the existing huge quantities would be a solution to the serious problem Black Sea confronts with. For estimate the potential of hydrogen based on the hydrogen sulphur from the depth layers of the Black sea, is necessary to know the temperature variation and the quantities of hydrogen sulphur from these layers. In figure 1 on present the temperature variation of the surface waters due to the season, but general interval is between –2^0C and 30^0C. Still, at over 150 m depth, (interesting areas) medium temperature is between 9-10^0C.

Table 1

Total H_2S production in the Black Sea

Zone		Total H_2S production 10^6 t/year	Burial in sediments 10^6 t/year	Flux from sediments 10^6 t/year
Water column	**Shallow water (<200 m)**	-	-	-
	Deep water (200-2200 m)	20.20	-	-
Sediments	**Shallow water**	7.89	0.14	7.75
	Deep water	5.53	0.28	5.25
Total		**33.92**	**0.42**	**13.00**

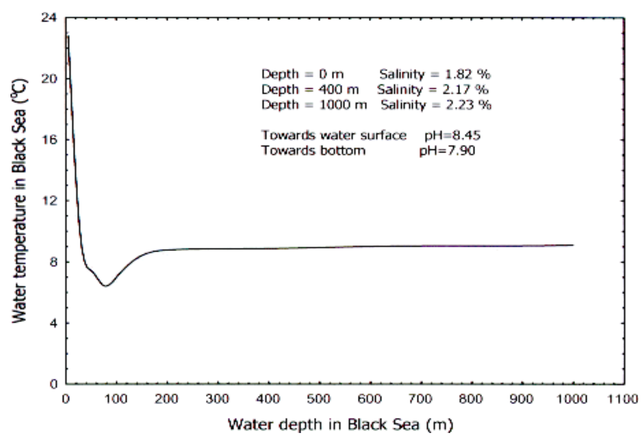

Fig.1 The dependence between temperature and the water depth in Black Sea

In figure 2 we present the variation of the hydrogen sulphide concentration in depth waters from the Black Sea, remark that specific references sources give until 30% H_2S concentration at depth to 2000 m (13,789 mg/l –Neretin et al.; 9,6 mg/l –Dimitrov et al.). Both assessment have be made using concentration simulation techniques between 100 m and 2000 m. These dates give information about the type of the potential obtained by H_2S from depth waters. Supplementary dates proves that the maximum hydrogen sulphur potential on surface is of 159,1 mol/m^2 between 1000 and 1500 m. In the same layer we can calculate maximum hydrogen sulphur potential that is about 1,469 x 10^9 tons, see figure 3. These results prove that the hydrogen is produced from layers with depth between 100 until 2000 m.

Considered theoretical efficiency of disintegration reaction of H_2S 100%, we can calculate the energetically potential of the hydrogen from the depth layers of Black Sea. Evaluate with Neretin et al.'s dates, we can determinate the variation of the hydrogen potential function of H_2S potential. In figure 4, we can observe that in layer from 100 m, the hydrogen potential from H_2S is virtually null, than, at 150 m we obtained 0,00266 x 10^{-2} g H_2 from 0,045 x 10^{-2} g H_2S , and at 2000 m we obtained 0,0816 x 10^{-2} g H_2S. With these dates we can calculate the potential of hydrogen in different layers from Black Sea waters.

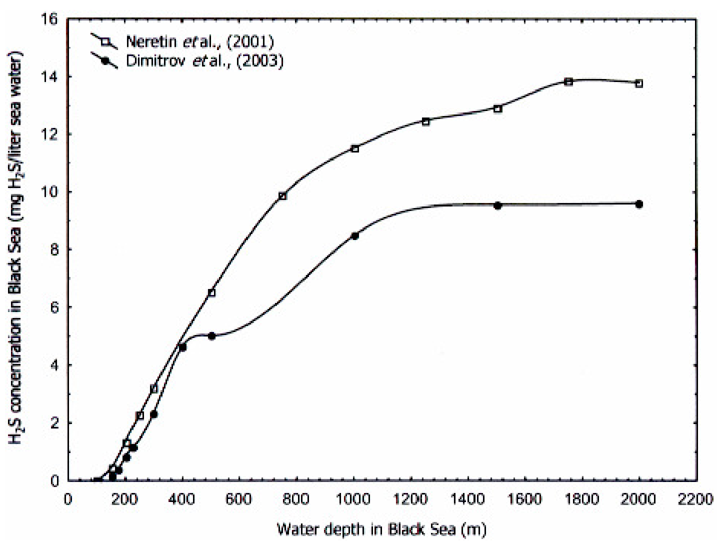

Fig. 2 The variation of H_2S concentration function of the depth water in Black Sea

In figure 5 we observe the maxim potential of hydrogen estimate at 86,411 x 10^6 tons of H_2 from 1,469 x 10^9 H_2S, in layer between 1000 m and 1500 m. Minimal values are between 100 m and 200 m. The total potential of hydrogen of the Black Sea estimate by this method is 270 x 10^6 H_2 from 4,587 x 10^9 H_2S in all

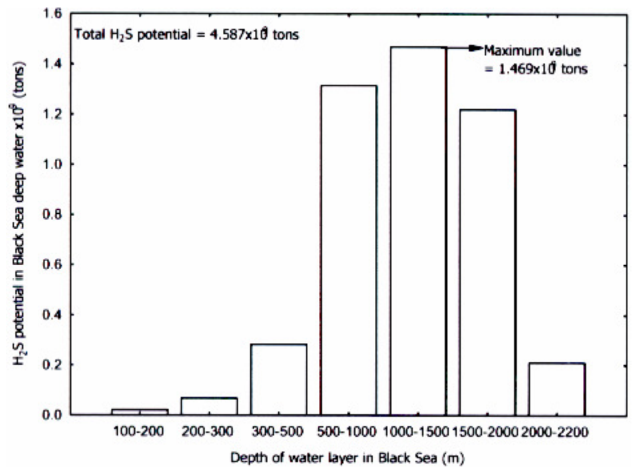

Fig. 3 Variation of the H_2S potential function of water depth in Black Sea

water layers of the Black Sea. Calculated values from the estimated quantity of hydrogen are 383 x 10^5 TJ for thermal energy or 89,7 x 10^5 GWh for electrical energy. By comparing we can say that 383 x 10^5 TJ of thermal energy is equivalent with 8080 x 10^5 tons of gasoline, 7660383 x 10^5 tons of natural gas, 8410 x 10^5 tons of fuel oil or 8510 x 10^5 tons natural oil.

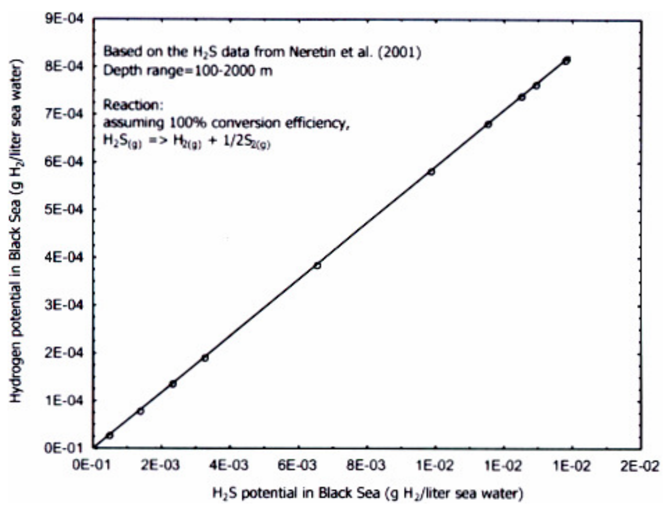

Fig.4 Potential of hydrogen variation function of de H_2S potential by Neretin et al.

Considering that on the Black Sea coast live 10 millions families and the required of energy is approximated to 36 billions kWh, the calculated potential of hydrogen transformed in electrical energy can be consumed in approximate 250 years (taking consideration the actual basin and only the depth waters).

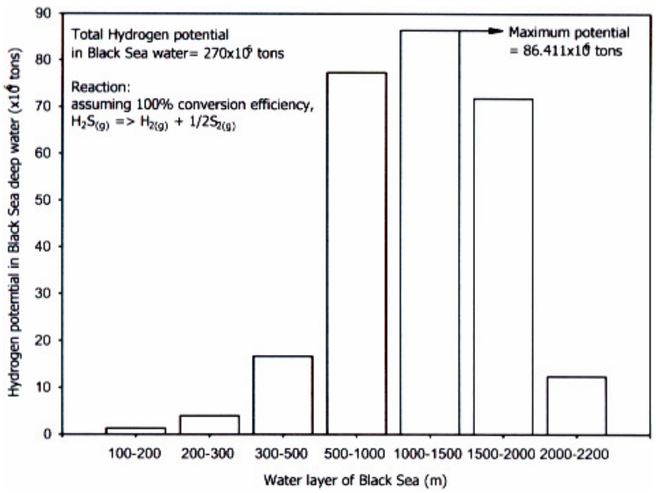

Fig. 5 Potential of hydrogen variation function of water layers of the Black Sea

3. Solutions for the hydrogen use

There are many methods for hydrogen obtaining from H2S disintegration. These technologies there are in different stages of development and may be classified as thermal technologies, thermo chemical, electrochemical photochemical and plasma technologies. Still in present there are not feasible commercial technologies for H_2 and sulphur produce by H_2S disintegration.

Thermal method [5][6] – is the most direct disintegration process of H_2S by catalytic or non-catalytic methods by means of high endothermic reactions. There are necessary studies for kinetic process and for established the used catalysts. **Thermo chemical method** [7] [8] [9] [10] **–** there are used some thermo chemical cycles devised or water decomposition involving H_2S decomposition phase which have conduce at independent cycles for hydrogen and sulphur produce. But the handle of large mass of sulphides and metals, also the repeat of cooling and heating process involve many complications.

Electro chemical method [11] [12] [13] – was made by water electrolyse to H_2S. It may be used direct or indirect electrolyse method. Principal problems consist in electrodes passivation (with sulphur) and secondary electrochemical reactions, also the difficult replacement of electrodes. It's an energo-intensive method.

Photochemical method – the H_2S and water photodisintegration is made by solar energy. There are necessary photo catalysts for the energy absorption by molecules. Their role is similar to the chlorophyll in photosynthesis process. The conversion level of actual technologies is limited

Plasma Method [14] [15] 6] **–** plasma results in electric process as microwave radiation and glow discharge as used for H2S dissolution. Solution is not much used being necessary electricity.

When the hydrogen purity is low, H2S may be used as direct gas in special construction SOFC.

4. Method for galvanic burning by electrochemical oxidation of H_2S

A new method for use H_2S as fuel propose the galvanic burning by electrochemical oxidation of H_2S. This method proposes asymmetric cells having only one active electrode described in figure 6. The cell asymmetry is required because the hydrogen sulphide is dissolved into the electrolyte (sea water) and the hydrogen sulphide oxidation occurs at the contact surface between the active electrode and the electrolyte.

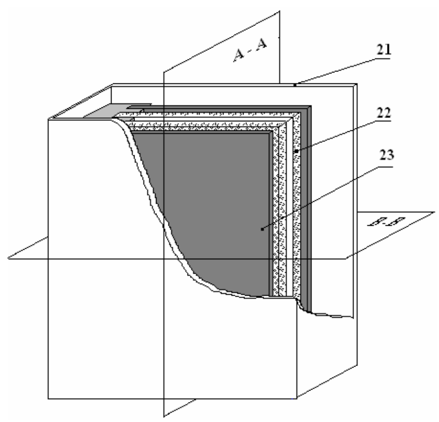

Figure 6. Rectangular cell [17]

The process generate electrical power in which hydrogen sulphide that is dissolved in a liquid electrolyte is electrochemically oxidized. The process proceeds in a pressurized environment (≥ 20 Barr) to prevent electrolyte + H_2S mixture from boiling and mobile electrolyte (sea water + H_2S minimum 0.01 n, 282 K). The supplying of oxygen is made through a porous electric conductive element having a catalyst loading, a strictly controlled pressure with respect to the reaction environment pressure being provided (Δp~15 mBarr). The oxidation of H_3O^+ and HS^- ions in the electrolyte at the surface of the porous element leads to charging positively the porous element and producing water and thermal energy that are dissipated into the electrolyte. A differential potential appears between a smooth anode and the porous element that acts as a cathode, the generating voltage being a function of the reaction environment parameters. Simultaneously with the oxidation, reactions of reduction of S^{2-} and OH^{-} take place at the surface of the anode, the elemental sulphur resulted being removed by the flowing of the electrolyte and H_2S mixture.

The described cell is part of submersible equipment designed for operation at maximum 800 m water depths.

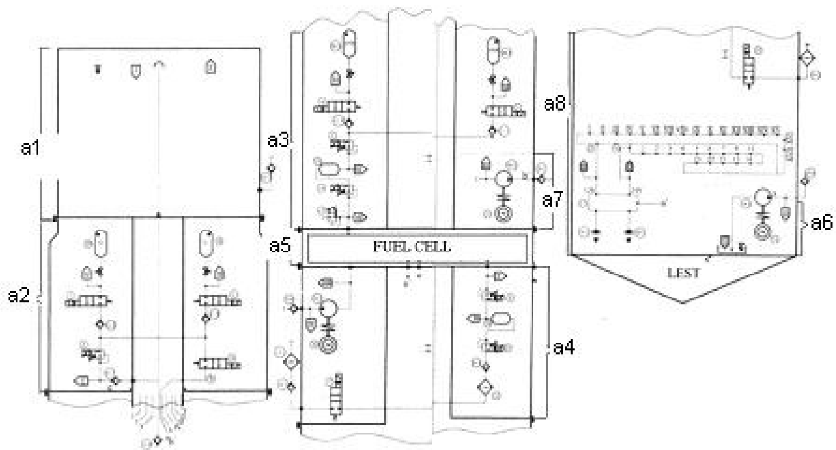

Fig. 7 Submersible equipment
(a1- floating compartment, a2- handle floating compartment, a3-technological air compartment, a4-barometric compartment, a5- combustion cell compartment, a6-technological water compartment, a7-hosting compartment, a8-santina compartment)

Submersible equipment in figure 7 is the experimental stand with proper energy source. The autonomic equipment will work by made proper electrical energy, containing a system for colloidal sulphur recovering from electrochemical reaction.

5. Conclusion

In present Black Sea is the biggest deposits of hydrogen sulphide of the earth, evaluate at $4{,}587 \times 10^{9}$ tons of H_2S in all water layers.

This particular case of the Black Sea has generated two ways of research: first to find solutions for H_2S disintegration in hydrogen, second find solution for reduced the rise level of H_2S, which can change in the next 30-40 years this sea in a no live sea. Also there is a supposition regarding the danger of a blast of H_2S due to a natural cataclysm or an accident witch modified the equilibrium between oxic and anoxic layers.

A theoretical evaluation based of disintegration of H_2S regarding the hydrogen production with 100% efficiency, will prove that the total quantity of H_2 from the Black Sea is 270×10^{6} tons. This H_2 quantity can assured the necessity of energy of 10 millions of families during 250 years. Actual solutions to obtained

H_2S with high concentration in layers at 1000 m and 1500 m depth has not commercial character. An original solution is a asymmetrical cell with only an electrode working at requested depth by it proper energy and storing the excess of energy.

Only the reduction of the H_2S from the Black Sea is not a sufficient research purpose, but the risk of the live disappeared must be an ecological purpose to continue the research. In this direction, the proposed combustion cell will carry out results regarding environment, in the worst case of a null energetic balance of working cell. So, the investment will be for the environment and will have a public investment character.

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