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CATALYTIC OXIDATION OF SULFIDE IONS IN BLACK SEA WATER

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Abstract

*The present study is an attempt for removal sulfides from the Black **S**ea water by their oxidation to sulfites or sulfates by heterogeneous catalysis. The experiments were carried out with sulfides at different initial concentrations within 25 and 125 g m^{-3}. The catalytic process is combined with electrochemical oxidation. Different catalysts were tested: activated carbon, zinc sulfide, cobalt sulfide and some other cobalt-containing and manganese-containing compounds.*

Best results were observed with spinel-type cobalt and manganese oxide included in an activated carbon matrix.

Key words: *Hydrogen sulfide, Oxidation, Catalysts, Fuel Cell*

1. INTRODUCTION

The Black **S**ea water contains significant quantity of hydrogen sulfide after depth of 150 m. Its amount is estimated to be around 4.6 billions tons (*Demirbas***,** 2009). Due to the very high toxicity of hydrogen sulfide, beneath this depth the sea is practically dead with exception of some sulfur metabolizing bacteria. The H_2S and other sulfur compounds are products of the anaerobic decomposition of sulfur-containing organic matter and nearly always present together in these natural processes (*U.S. National Research Council. 1979*). A lot of efforts are made to utilize and decompose them to harmless products (*Demirbas* 2009, *Ouali et al. 2011, Reddy et al. 2012).*

There are efforts to oxidize sulfide anions in a fuel cell, producing elemental sulfur in the anodic compartment (*Dutta et al., 2008*). In this case however, the electrodes could be easily passivated by the sulfur accumulation on the anode surface. Another disadvantage of these cells is the use of cyanoferrate as electron acceptor.

A possibility of using the oxidation energy of H_2S into a fuel cell is main goal of our team, cf. Fig. 1. The idea is to transform the sulfide species into sulfate ones, thus gaining more energy, returning harmless ions into the sea entering again into its natural cycle. The first step is to develop a process and to compose catalysts enabling the oxidation of sulfide to sulfite and sulfate ions and thus to avoid the accumulation of harmless elemental sulfur. The aim of the present paper is to study the catalytic oxidation of sulfide containing model solutions as a first step for construction of a highly effective fuel cell.

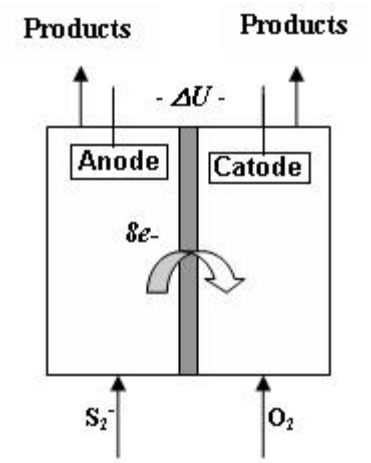


Fig 1. Scheme of a fuel cell

2. MATERAILS AND METHODS

Scheme of a fuel cell is shown in Fig 1. In this fuel cell, the following main anode and cathode reactions can take place.

$$\text{Anode: } S^{2-} + 8OH^- = SO_4^{2-} + 4H_2O + 8e^-$$

$$\text{Cathode: } 2O_2 + 8H^+ + 8e^- = 4H_2O$$

$$\text{The net reaction is: } S^{2-} + 2O_2 = SO_4^{2-}$$

The objective of the present paper is the reactions that take place into the anode space:

$$S^{2-} + 6OH^- = SO_3^{2-} + 3H_2O + 6e^-$$

$$\underline{SO_3^{2-} + 2OH^- = SO_4^{2} + H_2O + 2e^-}$$

$$\text{Total: } S^{2-} + 8OH^- = SO_4^{2-} + 4H_2O + 8e^-$$

The model solutions are prepared by dissolving of sodium sulfide nonahydrate, an ACS reagent ≥98 %. The salinity of the seawater is imitated by the dissolution of NaCl analytical grade into distillated water with concentration 16.5g l^{-1}.

The concentration of all sulfur containing reducing agents is determined iodometrically. The sulfide (S^{2-}) content is defined photometrically by its transformation to methylene blue *(Gustafsson 1960),* instead of the classical *N*,*N*-Dimethyl-*p*-phenylenediamine *N*,*N*-Diethyl-*p*-phenylenediamine was used as it was reported (*Rees et al. 1971*) to be two times more sensitive.

As the presence of thiosulfate ions inhibits the further oxidation of the sulfite ones (*Linek and Vacek, 1981*) the thiosulfate ions were detected qualitatively with Fe^{3+} by the appearance of the red, but not stable complex $Na[Fe(S_2O_3)_2]$.

Qualitative tests for sulfate (SO_4^{2-}) and sulfite (SO_3^{2-}) ions are also executed by adding $BaCl_2$. The opalescence or white deposit shows the presence of both species, but the sulfite ones are soluble in hydrochloric acid.

The presence of sulfite and sulfate ions is proved in all the experiments that were carried out. Elemental sulfur is not detected.

3. RESILTS AND DISCUTION

Several different sets of lab scale experiments are carried out varying the initial sulfide concentrations, type of catalysts and their concentration.

3.1. INFLUENCE OF THE INITIAL SULFIDE CONCENTRATION

Experiments with different initial concentration of 25, 70, 110 mg/l sulfide ions are carried out. A comparison of the decrease of the sulfide ions as a function of time is shown in Fig. 2.

As seen from the figure, the sulfide oxidation rate does not depend on the initial concentration. In all cases the reduction of the sulfide ions is about 50% at the second hour, about 80% at the fourth hour and 90% at the fifth hour.

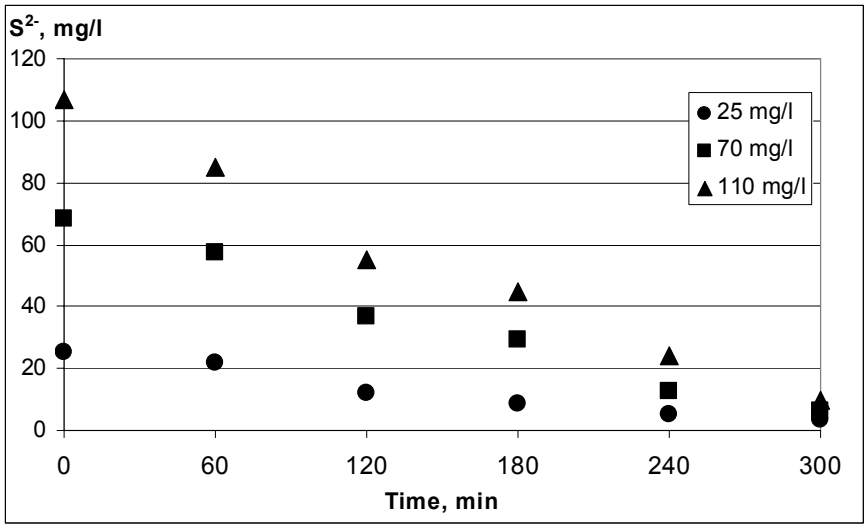


Fig 2. Influence of the initial sulfide concentration on the oxidation rate

3.2. OXIDATION WITH DIFFERENT TYPE OF CATHALYSTS ADDED INTO THE SOLUTION AS SALTS

As it is reported that different metals (*Dohnalek and FitzPatrick 1983*) are catalysts for the process of oxidation. In order to compare the catalytic effect of different Me^{2+} ions experiments with various salts directly introduced into the solution are carried out. The following species are used:

1. $CoCl_2$ with concentration of 0.5 $g.l^{-1}$;

2. Precipitate of CoS with concentration of 0.7 $mg.l^{-1}$;

3. ZnS with concentration of 0.5 $g.l^{-1}$;

The change of the concentration of the sulfides as a function of time with different catalysts is shown in Fig.3

It can be seen from the figure that the use of catalysts can considerably improve the velocity of the process. In case of absent of catalyst at a certain moment there is a significant retention of the oxidation rate that is due to the accumulation of the products and competitive reactions. In those experiment thiosulfates are observed with qualitative reaction. The catalyst accelerates not only the basic reaction, but also secondary reactions and thus prevents the accumulation of intermediates and the delay in the primary reaction. It is clearly seen from the figure that the use of catalysts leads to a constant oxidation rate.

As seen from the figure, cobalt containing catalysts give better results. The precipitate of CoS shows the best results. Unfortunately at the end of the process it has been dissolved. This fact limits its use as a catalyst.

3.3. OXIDATION WITH CATALYSTS OF DIFFERENT SPINEL-TYPE OXIDES INCLUDED INTO AN ACTIVATED CARBON MATRIX AS CATALYST.

In order to protect the catalyst from dissolving it into the solution and to prepare electrodes in the future, spinel-type of oxides included into an activated carbon matrix were prepared. The technology for obtaining such carbon matrix from organic-containing initial materials includes its impregnation with a solution of a given salt and the subsequent pyrolisys with simultaneous activation described in (*Ljutzkanov and Atanasov 2002*). Two different spinal-type oxides (Co_3O_4) and (Mn_3O_7) are prepared on the base of cobalt and manganese salts.

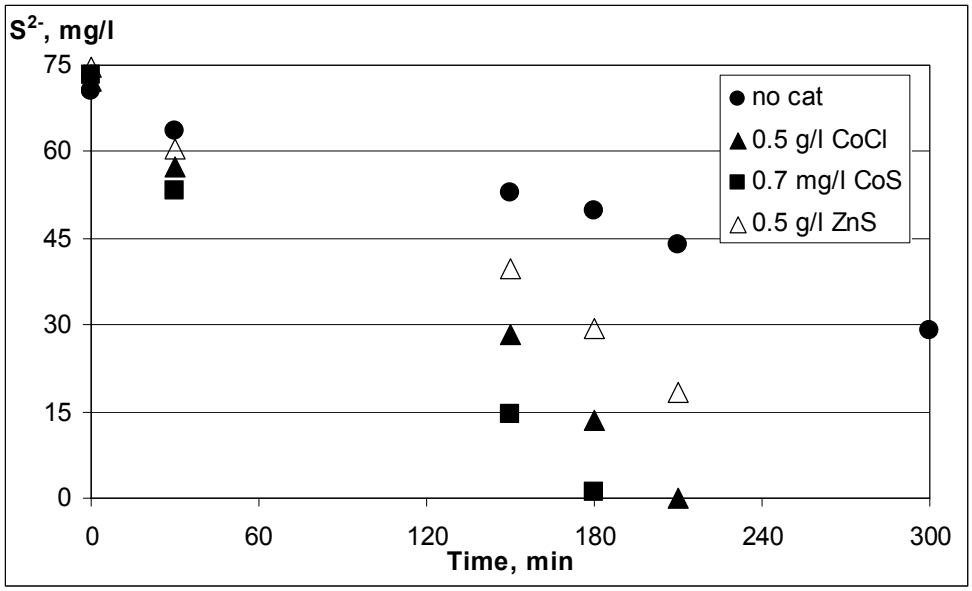


Fig 2. Influence of the different type of catalysts on the oxidation rate

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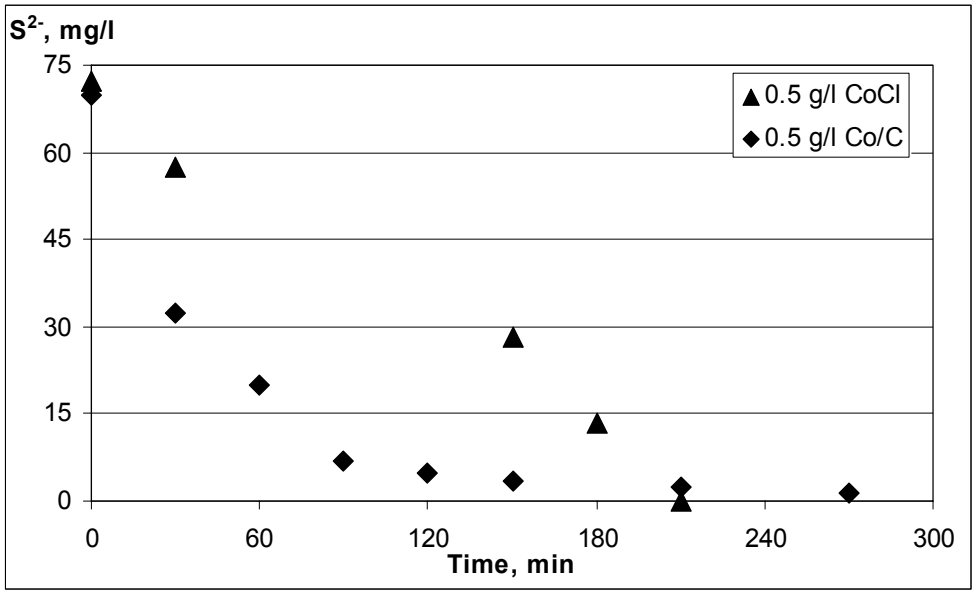


Fig. 3. Comparison between salt type and spinel type cobalt contain catalyst

Several different sets of lab scale experiments with spinel- type of oxides included into an activated carbon matrix are carried out varying the type of catalysts, their concentration and place of adding.

A comparison between the spinel – type cobalt containing oxides included into an activated carbon matrix and the $CoCl_2$ in same concentrations and added into the volume of the reactor is shown in Fig. 3.

As seen from the figure, the spinel – type cobalt containing catalyst give better results. Using this type of catalyst about 90% of the sulfide oxidation is achieved for 1.5 hours, while with the salt type cobalt containing catalyst there is only about 85% sulfide oxidation for 2.5 hours.

A comparison of the rate of the decrement of the sulfide concentration with time for a process without catalyst and with both type of spinal-type oxides added in the solution is presented in Fig. 4. There is a significant difference between the catalyzed and the non-catalyzed process. The activated carbon matrix with incorporated cobalt shows a slight superiority to the one with manganese.

Experiments with different quantities of spinel – type cobalt containing catalyst added into the volume of the reactor are conducted. Fig. 5. illustrates the influence of the amount of the catalysts that is used. This indicates that the increase in the amount of the catalyst with 30% giving acceleration of the sulfide oxidation rate with about 5%, i.e. there is no significant impact on the process.

In order to use the catalyst continuously and to gain some experience for the technology of electrode manufacturing, experiments with fixed catalyst were carried out.

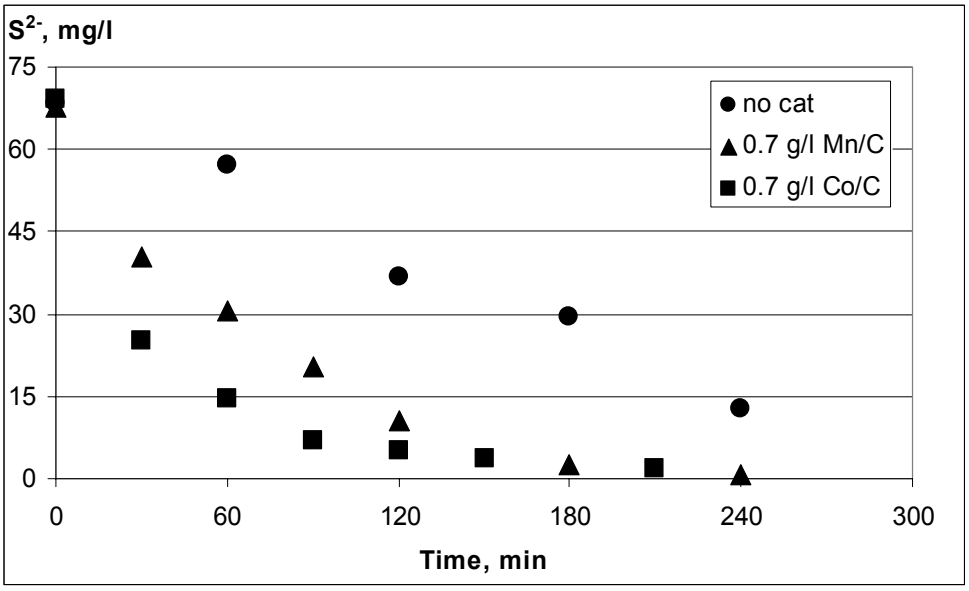


Fig.4 Influence of the different spinel-type oxides incorporated into an activated carbon matrix catalysts on the oxidation rate

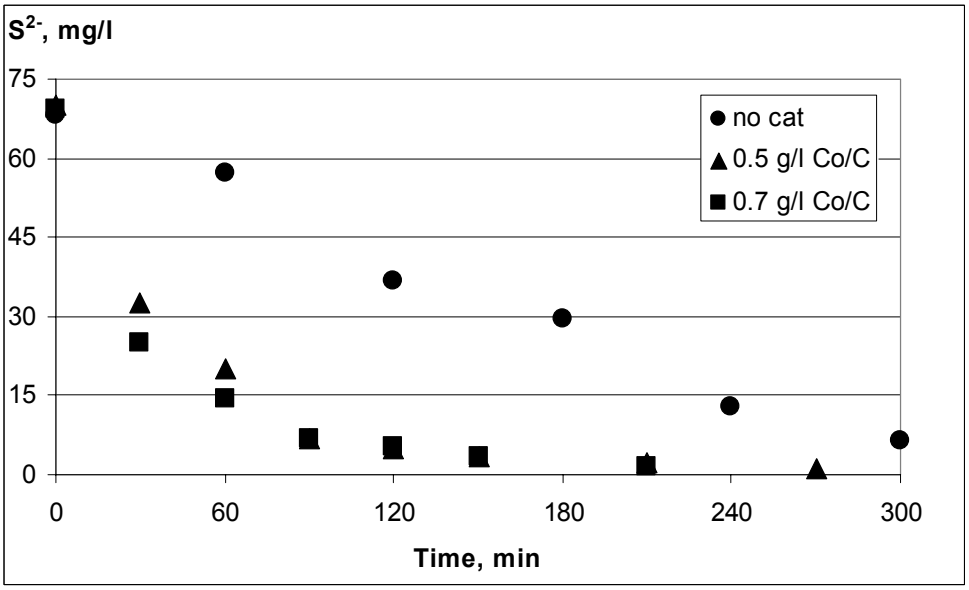


Fig. 5. Influence of the quantity of the added catalyst

A comparison of the sulfide oxidation rate with fixed and added into the volume of the solution catalyst is given in Fig. 6.

As seen from the figure, the fixed catalyst gives better results. In this case about 95% of the sulfide is oxidized for the first hour, whiles with free catalyst there is only about 80% sulfide oxidation for the

same time, although in the fixed catalyst the interfacial surface is considerably diminished. This gives the conviction that the used materials could be successfully used for electrode manufacturing.

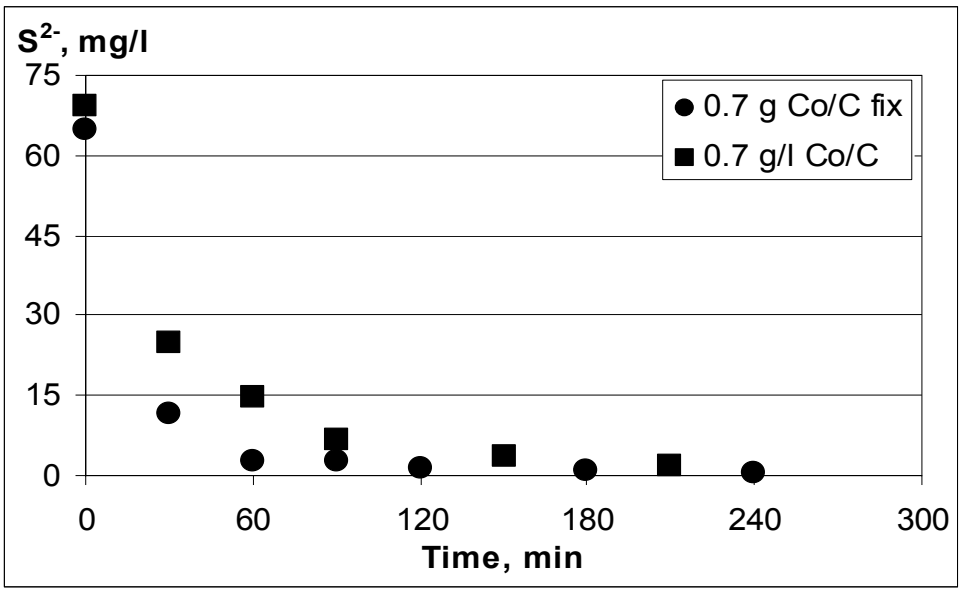


Fig. 6. Comparison between fixed and added into the volume of the reactor catalyst.

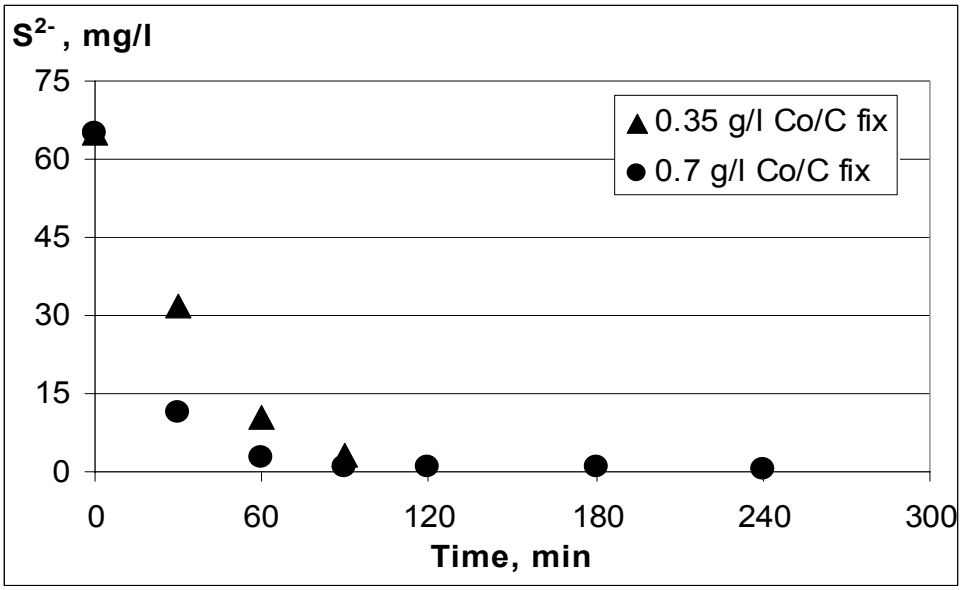


Fig.7. Influence of the quantity of the fixed catalyst

A comparison of the sulfide oxidation rate with different quantity of fixed catalyst is given in Fig. 7. As expected, large amount of catalyst gives a high sulfide oxidation rate.

4. CONCLUSIONS

The hydrogen sulfide from the deep Black sea waters can be successfully removed by oxidation to sulfites or sulfates by heterogeneous catalysis. The use of catalysts can enhance considerably the process rate. At a certain moment there is a significant retention of the oxidation rate in case of absence of catalyst. Probably it is due to the accumulation of the products and competitive reactions as obtaining of thiosulfates. The catalyst accelerates not only the basic reaction, but also secondary reactions and thus prevents the accumulation of intermediates and the delay in the primary reaction. Its use leads to a constant oxidation rate.

Among the examined catalysts the best ones are those containing cobalt. Entirely new spinel-type catalyst, incorporated into an activated carbon matrix has been synthesized.

Experiments with fixed catalyst have been successfully carried out and the sulfides can be reduced by over 90% within 2 hours. The latter can be used in future for electrode manufacturing.

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REFERENCES

Demirbas A., (2009), Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, Volume 31, Issue 20, Hydrogen Sulfide from the Black Sea for Hydrogen Production, 1866-1872

Dohnalek, D.A. and FitzPatrick, J.A. (1983)The chemistry of reduced sulphur species and their removal from groundwater supplies. J. Am.Water Works Assoc., 6: 298.

Dutta Paritam K., Korneel Rabaey, Zhiguo Yuan, Jürg Keller, (2008), Spontaneous electrochemical removal of aqueous sulfide, Water Research 42, 4965 – 4975

Gustafsson L. (1960), Talanta, 4, 227-236

Linek, V. and Vacek, V., (1981), Chemical engineering use of catalyzed sulfite oxidation kinetics for the determination of mass transfer characteristics of gas liquid contactors.*Chem. Engn 9 Sci.* 36, 1747-1768.

Ljutzkanov L., Atanasov A., Method for Treatment of Carbon-Containing Materials, BG patent **№** 63594 /26.06.2002.

Ouali Salima, Samira Chader, Maïouf Belhamel, Mebrouk Benziada, (2011), The exploitation of hydrogen sulfide for hydrogen production in geothermal areas, International Journal of Hydrogen Energy 36 4103 -4109

Rees T. D., Gyllenpetz A. B., Dochery A. C., (1971), Analyst, 96, 201.

Reddy E. Linga, V.M. Biju , Ch. Subrahmanyam , (2012) Production of hydrogen from hydrogen sulfide assisted by dielectric barrier discharge, Interational Journal of Hydrogen Energy 37 2204-2209

U.S. National Research Council. (1979). Hydrogen sulphide. Committee on Medical and Biologic Effects of Environmental Pollutants, Subcommittee on Hydrogen Sulphide. University Park Press, Baltimore, MD