

## Contaminated Sulfide Waste Water - Negative Impact on Human Health and the Environment

Eleonora Butenko\*

*Priazovskiy State Technical University, Mariupol, Ukraine*

**\*Corresponding Author:** Eleonora Butenko, Priazovskiy State Technical University, Mariupol, Ukraine.

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### Abstract

The sources of sulfides formation, their harm to the environment and human health were studied; proposed methods and fundamentals of technologies for the removal of sulfides from industrial wastewater.

**Keywords:** *Hydrogen Sulfide; Sulfides; Toxicity; Industrial Pollution*

Hydrogen sulfide and sulfides in general belong to the second category of hazard. They are toxic and inhalation of air contaminated with hydrogen sulfide causes dizziness, headache, nausea, and in case of substantial concentration of hydrogen sulfide may lead to coma, convulsions, pulmonary edema, and even death. At high concentrations, a single inhalation can cause instant death.

The main damage to the environment is caused by the oxidation of hydrogen sulfide and sulfides with oxygen soluble in water, which results in the lack of oxygen in water, and thus the death of the flora and fauna.

Reacting with metals, hydrogen sulfide causes corrosion of the telecommunication facilities, and reacting with iron, it forms iron sulfide or FeS, which precipitates on the surface of pipes and reduce their channel capacity.

### Physicochemical and toxicological properties of sulfides

The most detailed information on physicochemical and toxicological properties of sulfides is described in the normative document of the World Health Organization (WHO) [1,2].

#### Physicochemical properties [1]

Colorless gas, m.p = -85.5°C, b.p. = -60.7°C, density = 1.54 g/L at 0°C, solubility in water: 4370 ml/L (0°C); 1860 ml/L (40°C), vapor pressure 1875 kPa at 20°C.

#### Organoleptic properties [3-5]

Hydrogen sulfide has the characteristic odor of rotten eggs, which can be detected even at very low concentration below 8 µg/m<sup>3</sup>. At the concentration of 50 - 150 µg/m<sup>3</sup> in air hydrogen sulfide has slightly sweetish odor, and at higher concentrations the sense of odor is diluted. In water, the taste and odor concentration threshold is estimated to be from 0.05 to 0.1 mg/L.

#### Hydrogen sulfide conversion in the environment [6,7]

In nature, hydrogen sulfide is formed upon sulfide hydrolysis in water. In an aqueous medium, sulfides undergo dissociation and step-wise hydrolysis, as a result of which both HS<sup>-</sup> and S<sup>2-</sup> ions are present in water. The ratio of these forms depends on the pH of the medium.

At pH = 7.4, approximately one third of it is the undissociated hydrogen sulfide, and the rest is hydrosulfide. Sulfides in appreciable concentrations appear at pH higher than 10.

### Uses of sulfides

The industrial applications of hydrogen sulfides are to produce sulfuric acid, various inorganic sulfides, thiophenes and mercaptans, thiols, thioaldehydes, and thioketones. Derivatives of hydrogen sulfide are employed in the manufacture of dyes, in the leather industry, in wood processing, and cosmetic industry. Sulfide-containing mineral waters can be used for therapeutic baths. In analytical chemistry, hydrogen sulfide often serves as a reagent for the deposition of heavy metals which sulfides are poorly soluble in water. In aerated natural water, hydrogen sulfide is easily oxidized to sulfites. Biological oxidation proceeds to elemental sulfur. Under anaerobic conditions, the reverse process of reduction to molecular sulfur and sulfides can be observed.

### Impact on the environment and human health

Hydrogen sulfide is constantly present in the atmospheric air as a result of natural emissions, with concentrations ranging from 0.1 to 1  $\mu\text{g}/\text{m}^3$ . However, in the areas of industrial pollution, these concentrations exceed 100  $\mu\text{g}/\text{m}^3$  [8-10].

Most of the hydrogen sulfide present in water comes from industrial pollution. In groundwaters, the concentration of hydrogen sulfide mostly depends on the mineralogical composition of the rocks and the microorganisms which are present in the water. The highest concentration recorded in underground water exceeds 500  $\mu\text{g}/\text{l}$  [11].

Hydrogen sulfide and soluble alkali metal sulfides can be rapidly absorbed after ingestion. The main paths of their redistribution in the body are *via* brain, liver, kidneys, and pancreas. Metabolism occurs mainly in the liver and proceeds in two directions - oxidation to sulfite and methylation to form methanethiol and dimethyl sulfide. Sulfides and sulfites are rapidly excreted through the kidneys, and a small fraction is excreted through the lungs. For humans, the deadly oral dose of sodium sulfide is estimated at 10 - 15g. When inhaled, hydrogen sulfide is highly toxic to humans. The high rate of toxicity is determined by the formation of a complex with an iron (III) ion, which blocks the oxidative process. Eye and respiratory irritation is observed at concentrations of 15 - 30  $\text{mg}/\text{m}^3$ ; hydrogen sulfide at concentrations of 700 - 1400  $\text{mg}/\text{m}^3$  may lead to respiratory paralysis and death.

The threshold limit value of hydrogen sulfide are 10  $\text{mg}/\text{m}^3$  in the working area; short-term exposure limit is 0.008  $\text{mg}/\text{m}^3$ ; the average daily limit is 0.008  $\text{mg}/\text{m}^3$ .

The threshold limit value of hydrogen sulfide mixtures with hydrocarbons is 3  $\text{mg}/\text{m}^3$  and with air of in the populated areas is 0.008  $\text{mg}/\text{m}^3$ . Tangible smell of hydrogen sulfide is observed at the concentration of 1.4 - 2.3  $\text{mg}/\text{m}^3$ ; a significant smell - at 4  $\text{mg}/\text{m}^3$ ; a heavy smell at 7 - 11  $\text{mg}/\text{m}^3$ . At high concentrations above 1  $\text{g}/\text{m}^3$  poisoning occurs instantly, causing convulsions and loss of consciousness, death occurs due to paralysis of the respiratory system.

Hydrogen sulfide is a strong nerve poison. The threshold of sensation of hydrogen sulfide odor in humans corresponds to 1 - 10  $\text{mg}/\text{m}^3$ . At 4  $\text{mg}/\text{m}^3$  there is a significant odor, and at the concentration of 6  $\text{mg}/\text{m}^3$  and inhalation time of 4 hours, headache and eye pain may occur. Eyes burning, redness, and swelling of the eyelids are among the indicators to increased hydrogen sulfide concentration (Table 1). In a mixture with hydrocarbons, the toxic effect of hydrogen sulfide is enhanced, which is why the threshold limit value of 3  $\text{mg}/\text{m}^3$  is recorded for such mixtures.

H <sub>2</sub> S, ppm	Exposure time
< 100	Few hours without any problems
> 100	60 minutes without serious problems
> 500	30 minutes - life threatening
> 1000	Danger to life within a few minutes
> 5000	Life threatening for a few seconds

**Table 1:** Human expose threshold.

### Sources of sulfide pollution

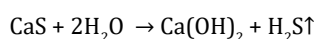
The source of sulfides in surface water is the reduction process which occurs upon bacterial decomposition and biochemical oxidation of organic natural compounds, and substances entering the reservoir with industrial wastewater.

Sulfide-containing industrial wastewater is a significant source of environmental pollution [12]. As of today, the amount of sulfide-containing wastewater is estimated to be at 65 million m<sup>3</sup> per year with the concentration 100 to 500 mg/l.

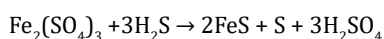
Particularly severe water pollution with sulfides is observed in the places of storage of sulfide ores dumps and metallurgical slag [13].

Microorganisms can form hydrogen sulfide in the slag heaps, the total amount of which may exceed 20m<sup>3</sup> per ton of slag. Basically, the sulfide solutions with an extremely high concentration of hydrogen sulfide are formed, which are then washed out by drainage water, which results in the most severe pollution of waterbodies. Therefore, it is absolutely crucial to prevent sulfides from entering the water basin.

Calcium sulfide decomposes upon contact with water, including moist air, resulting in calcium hydroxide and hydrogen sulfide gas formation:



Purification of sulfide-polluted wastewater can be carried out by various methods [14], which include oxidation, conversion of sulfides into hydrosulfides, precipitation, and sorption. The most optimal and effective way to lower the concentration of sulfides is to use iron salts, which form insoluble iron sulfide and molecular sulfur, which preclude sulfides from entering the gas phase.



This method is more effective than introduction of oxygen gas into the liquid phase or pH adjustment. The prevention of the biological formation of sulfides in industrial dumps can be achieved by creating unbearable conditions for the existence of sulfate-reducing bacteria.

### Conclusion

Sulfides are hazardous compounds that have a negative impact on both the environment and human health. Sulfide contamination can occur both naturally and as industrial pollution. The most severe sulfide pollution is observed in the locations of non-ferrous and ferrous metallurgy enterprises. There are various methods of purification of wastewater from sulfides, and the most effective ones are the deposition and oxidation.

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### Bibliography

1. "Hydrogen sulfide". Geneva, World Health Organization, (Environmental Health Criteria, No. 19) (1981): 21.
2. Macaluso P. "Hydrogen sulphide". In: Encyclopedia of chemical technology. Volume 19, 2<sup>nd</sup> edition. New York: John Wiley (1969): 375.
3. Air quality guidelines for Europe. Copenhagen, WHO Regional Office for Europe (1987): 288.
4. Patwardhan SA and Abhyankar SM. "Toxic and hazardous gases. IV". *Colourage* 35.12 (1988): 15-18.
5. National Health and Welfare Canada. Guidelines for Canadian drinking-water quality - supporting documentation. Ottawa (1978): 32.
6. US National Research Council. Subcommittee on hydrogen sulfide. Baltimore, MD, University Park Press (1979): 9.

7. Mance G., *et al.* "Proposed environmental quality standards for List 11 substances in water: sulphide. Medmenham". Water Research Centre (ESSL, TR 257) (1988): 221.
8. Carpenter AB. "Influence of mineralogy and microorganisms on iron and sulfide concentrations in groundwater". US National Technical Information Service (1971): 578-609.
9. Torrans EL and Clemens HP. "Physiological and biochemical effects of acute exposure of fish to hydrogen sulfide". *Comparative Biochemistry and Physiology* 71.2 (1982): 183-190.
10. Kraft AA, *et al.* "Detection of hydrogen sulfide in packaged meats and in broken out shell eggs". *Food Technology* 10 (1956): 443-444.
11. T Bagarinao and Vetter RD. "Sulfide tolerance and detoxification in shallow-water marine fishes". *Marine Biology* 103.3 (1989): 291-302.
12. E Butenko and A Kapustin. "Water pollution in the Mariupol industrial region". *Ecology and Industry* 3 (2011): 33-37.
13. Dan., *et al.* "Methods of reducing the impact of waste water of metallurgical and coke production on the environment of surface water and the waters of Azov sea". *Eastern European Scientific Journal* 4 (2015): 48-53.
14. E Butenko and A Kapustin. "Technology of removal sulfides". *East European Journal of Advanced Technology* 3/8.45 (2010): 7-9.

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