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A method for hydrogen sulfide removal in air of submarine by Lewatit TP 208

Denizaltı havasında hidrojen sülfitin Lewatit TP 208 ile giderilmesi için bir metot

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Abstract

In this paper is proposed a method to remove the hydrogen sulfide in air of submarine. This method is based on the absorption of hydrogen sulfide by Lewatit TP 208. Soda lime cartilage is commonly used in submarine for removing of moisture and carbon dioxide in air. In this process soda lime cartilage was combined with Lewatit TP 208. The amount of Lewatit TP 208 required for 710 m^3 air of submarine was 11 kg. The problem for submarine is hydrogen sulfide contents of seawater during in submerged condition. The proposal technique can remove of moisture and hydrogen sulfide in air of submarine. This process is the first record to remove the hydrogen sulfide in air of submarine.

Keywords: Hydrogen sulfide, toxicity, in air, Lewatit TP 208, submarine air.

Introduction

Hydrogen sulfide is a colorless gas, slightly heavier than air and moderately soluble in water. Hydrogen sulfide has a disagreable odour and may easily be detected in environment. It is flammable gas and burns in the air to give water and sulfur dioxide. The mixture of air and hydrogen sulfide in ratio 4.5% is explosive.

Hydrogen sulfide can be detected in air at concentrations of less than 0.1 μg/L (Cohn et al. 1999). The detection limit in the open air over a sample is approximately to 5 ppb and in close 2 ppb.

Sulfur compounds were found in seawater in inorganic form as: S^0, S^8, sulfate, thiosulfate, tetrathionate, hydrogen sulfide, sulfates, ferrosulfate, ferrosulfide, ferrisulfide, various metallic sulfides and in organic form; dimethylsulfide, dimethyl sulfoxide, dimethyl β propiothetine (dimethyl sulphoniopropionate, DMSP). Oxidation product of sulfide in sea water is thiosulfate. The oxidation of hydrogen sulfide in sea water is 0.35 g/m^3 in summer 70 g/m^2/years, and it reduction 25 g/m^2/year. In sediment 3.5-5.2 g sulfide yr^{-1} is produced by reduction of sulfate.

Hydrogen sulfide in water and sediments converts to less stable reduced sulfur compounds enriched in the deposits (Volkov 1991).

Sulfide is produced in sediment and many species of fish living in association with the bottom. The cytochrom C oxidase of all species of marine organisms shows high activity and susceptibility to sulfide poisoning, with 50% inhibition at 30- 500 nm in various tissues whereas all species have sulfide-oxidizing activity in blood, spleen, kidney, liver and gills, fish bloods have a high sulfide-oxidizing activity (Bagarinao and Vetter 1989).

Hydrogen sulfide can be produced by oxidation of sulfur compounds such as sulfate, sulfide, thiosulfate and presents in industrial and municipal waste water. Industrial paper plants using the Kraft process and leather industry uses sodium sulfide to remove the hair from hides prior to tanning are the cause of hydrogen sulfide pollution.

The toxicity of hydrogen sulfide

Hydrogen sulfide which is very poisonous when inhaled, in a larger amount causes headache, nausea. It may cause the person breathing and then collapse suddenly. Chronic exposure to low concentrations may produce conjunctivitis, photophobia, corneal bullae, tearing, pain, and blurred vision are the commonest findings (Klaasen et al. 1986). Hydrogen sulfide is irritant upper respiratory tract and eyes, asphyxiant, and can cause the pulmonary edema, affection nervous system, dizziness excitement, staggering ail, diarrhea, dysuria, bronchitis, bronchopneumonia, depression and at high concentrations are instantly fatal (Sax 1984).

Asphyxiant action hydrogen sulfide is due to paralysis of the respiratory center.

The hydrogen sulfide anion forms a complex with methemoglobin known as sulfmethemoglobin which is analogous to cyanohemoglobin.

Concentration of hydrogen sulfide in air as low as 0.006% are fatal if breathed for 30 min (Ehret 1960). In air 0.003% concentration causes anesthesia.

Threshold limit value (TLV) is 10 ppm in air.

Sulfur cycle

Sulfur cycle in nature is plant protein → animal protein → hydrogen sulfide → free sulfur → sulfuric acid → sulfate → plant protein (Beaver 1958).

Hydrogen sulfide is formed from the anaerobic decomposition of organic matter containing sulfur or by reduction of mineral sulfite and sulfate in marine environment. Hydrogen sulfide may be produced in sea water from reduction of sulfate ions by bacteria.

The bacteria involved in natural sulfur cycle are: (Fisher 1988)

1. Anaerobic dissimilatory sulfate reduction

Desulfotomaculum, Desulfomonas, Desulfovibrio, Desulfobacter, Desulfobulbus, Desulfococcus, Desulfosarcina.

2. Anaerobic dissimilatory sulfur reduction

Desulfovibrio, Campylobacter, Desulfomonas, Beggiatoa.

3. Anaerobic phototrophic sulfur oxidation

Some *cyanobacteria*

4. Aerobic chemotrophic sulfur oxidation

Thiobacillus, Sulfolobus, Thermothrix, Paracoccus, Pseudomonas, Beggiatoa, Thiothrix, Thiospira, Thioploca, Achromatium, Thiobacterium.

5. Anaerobic chemotrophic sulfur oxidation

Thiobacillus denitrificans, Thiomicrospira denitrificans.

Besides these bacteria, *Archaebacteria* and *Rhodospirillacea* group contribute also to sulfur cycle.

Hydrogen sulfide in the Black Sea

The Black Sea is largest anoxic basin and one of the rare reservoirs with constant and powerful hydrogen sulfide pollution in deep water. Hydrogen sulfide has been appeared in the Black Sea 7000-8000 years ago (Volkov 1991). According to Neretin (2003) the origin of hydrogen sulfide in the Black Sea were investigated by various authors, earlier views of Lebedintzov (1892), Zelinski (1893), Egunov (1900-1901), Andrusov (1894) Donilchenko and Chigirin (1926). These authors are suggested the origin of hydrogen sulfide was decomposition of organic compounds.

Hydrogen sulfides production from microbial sulfate reduction was first found by Zeliniski and Brulsiloski in 1893 (Vyazilov and Mikhailov 1991). In the Black Sea water the amount of hydrogen sulfide depends on depth. The total sulfide inventory on the contemporary Black Sea is about 4.6x103 Tg, the main part being located between 500 and 2000 m. Hydrogen sulfide zone was not the same in all part of the Black Sea. Hydrogen sulfide increases quasi linearly from 150-200 m to about 600 m with an almost constant gradient (0.13- 0.15 mg/L at each 10 m). Then the gradient is getting less, hydrogen sulfide amounts 10- 11 mg/L at 1000 m, 12-14 mg/L at 2000 m (Neretin 2003). The annual average hydrogen sulfide concentration in bottom water is 370 µM (Neretin 1996). Hydrogen sulfide distribution in sediment is not similar (Volkov 1991). Vertical distribution of temperature, salinity, and diversity in the Black Sea correlate with the sulfide vertical distribution (Neretin and Volkov 1995 a, b).

According to Vyazilov and Mikhailov (1991) the first oceanographic observation of current in Bosphorus was done by Makarov in 1881-1882, owing to which the existence of the two layer current was establish on the surface from the Black sea to the Sea of Marmara and the bottom current in opposite direction. Sea water amount enter to Istanbul Strait (Bosphorus) from the Black Sea 120- 312 km^3/year.

Water exchange via the Bosphorus determines the formation of very complicated vertical water structure in the Black Sea. Hydrogen sulfide zone, layer of oxygen and hydrogen sulfide coexistence are important of ventilation process in the Black Sea anoxic zone, the Bosphorus flux can not be considered as a main factor for deep ventilation as suggested by the sulfide budget (Neretin 2003). Sulfide oxidation rate in the Black Sea chemocline yield and integrated value are 53 and 125 Tg yr^{-1} (Sorokin 1972, 1983).

Hydrogen sulfide formation in the Black Sea is increased in August and September.

Through the equation of $H_2S+2O_2 \longrightarrow SO_4^{-2}+2H$, the oxidation to sulfate in Istanbul Strait was calculated as 4.4- 9.2 Tg/year.

Table 1 shows hydrogen sulfide concentration in the Black Sea.

Table 1. Hydrogen sulfide concentration in the Black Sea (ml/L) (Danilchenko and Chigirin 1926).

Depth	**H_2S**
150	0.088
200	0.470
300	1.480
500	3.779
1000	5.637
1500	6.169
2000	5.796

In the Sea of Marmara, sulfur compounds detected were sulfur, dimethylsulfide, trisulfide dimethyl, dimethylsulfoxide, dimethylsulfone, and propiothetine (Güven et al. unpublished data).

Analysis of hydrogen sulfide

Hydrogen sulfide was detected by lead acetate (black flack), zinc acetate (white residue) and potassium antimonytartarate (yellow). Determination of hydrogen sulfide was made by various methods as spectrometrically by methylene blue method (Standard Methods 1995), gas chromotography (Ichinose et al. 1984) and capillary isotachophoresis (Fukushi and Hiiro 1987).

Removal of hydrogen sulfide

The chemical and bacteriological methods were used for the removal of hydrogen sulfide in wastewater (Metcalf and Eddy 2004). These techniques are summarized as:

1. *Biological removal*

Biofilters are packed bed filters.Microorganisms, bacteria, actinomycetes and fungi attached to the packing material.

Biotrickling filters. It is the same as biofilters with the some exception.

Conventional biological treatment processes. Microorganisms to oxidize hydrogen sulfide dissolved in liquid under aerobic conditions.

2. *Removal with chemical*

Chemical scrubbers are to provide contact between air, water and chemicals. It is based on oxidation or entrainment of the odorous compounds. In the single scrubbers, the scrubbing fluid sodium hypochlorite, hydrogen peroxide, potassium permanganate is circulated. Sodium hydroxide also used in this method. The end product of this process is $NH_2SO_4/S^0/K_2SO_4$. In this process the expected removal efficiency is 98% for hydrogen sulfide, 95% for sulfur dioxide.

Hydrogen sulfide in air of submarine

Hydrogen sulfide is important for air of submarine especially in the Black Sea. The tanks of submarine take water from the Black Sea. Hydrogen sulfide content of the Black Sea water is a cause of contamination in submarine air.

At the present in submarine, soda lime Drager packed-bed uses for removing of moisture in air.

Soda lime is a mixture of calcium hydroxide with sodium or potassium hydroxide intended for the absorption of carbon dioxide and water vapor in air.

In this work, the substance used for removal of hydrogen sulfide is Lewatit TP 208 (Bayer, Germany). The properties recorded in the prospect of Lewatit TP 208 are: It is cross linked polystyrene functional group iminodi acetic acid; appearance beige, opaque; water retention 55-60%; boat size 90% 0.4-1.25 mm; effective size 0.55; bulk density 1.17. It is weakly acidic, macroporous cation exchange resine with chelating cation. It removes the heavy metal cations from neutralized effluents but does not remove metals from solution containing EDTA or NTA.

The removal of hydrogen sulfide in submarine is important for health of submariner when it is submerged.

In this paper a method was proposed for the removal of hydrogen sulfide in submarine air.

Material and Method

The methods in this experiment use for removal of hydrogen sulfide in air are:

Process 1

Packing material: Lewatit TP 208 (Bayer, AG Chemical Leverkusen, Germany) and Bindungs patrone soda lime bed (Drager Sicherheits Technik GmbH, Lubeck, Germany).

1. *Experiment for removing hydrogen sulfide by Lewatit TP 208*

Figure 1 shows the experiment for proving of efficacy of Lewatit TP 208 for removing of hydrogen sulfide in air.

0.45 g sodium sulfur was placed in the flask with three necks. One of the neck was connected with a pipe to tube containing Lewatit TP 208 and Soda lime, second neck was attached a dropping funnel containing sulfuric acid 98%. The third neck connected to a pump for entrainment of hydrogen sulfide formed to the absorber containing tube.

The tube length is 30 cm, and 1 cm diameter, was filled as 5 cm coil Lewatit TP 208, and 5 cm of coil soda lime successively. The amount of absorbent for each coil was 10 g.

Sulfuric acid was dropped on sodium sulfur and formed hydrogen sulfide gas pass through the tube containing absorbers as indicated above. For the control of exhausted gas, pass to in lead acetate solution of 2% put at washing flask.

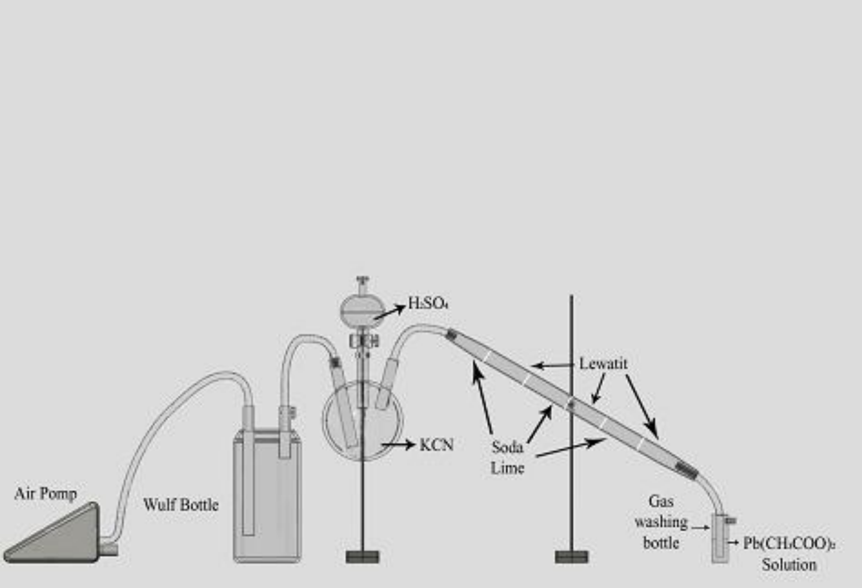

Figure 1. The scheme of experimental system for proving of hydrogen sulfide removal.

2. *The proposed cartilage unit for removing of hydrogen sulfide in submarine air*

The cartilage contains six cells by horizontal axis. Lewatit TP 208 and soda lime are placed successively in this packed bed as soda lime- Lewatit TP 208, soda lime- Lewatit TP 208, soda lime- Lewatit TP 208.

The cartilage capacity has over 5 kg.

The air can be passed through beds of Lewatit TP 208 and soda lime to remove of hydrogen sulfide and moisture.

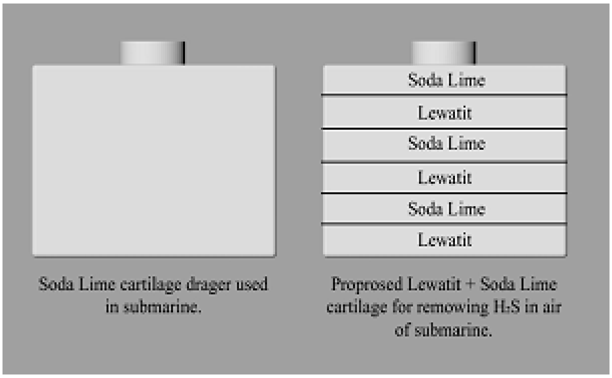

Figure 2. The designed of cartilage scheme.

Process 2

The air passed from:

2.1. Wet filter impregned lead acetate solution (10%).

2.2. Zinc acetate solution (25%) in wash bottle.

Results and Discussion

The hydrogen sulfide gas formed after reaction of the sulfuric acid and potassium sulfur was passed to tube containing adsorbents Lewatit TP 208 and soda lime column.

The exhanced gas was not given a reaction with lead acetate in washing bottle.

The experiment only soda lime absorber was not given positive results for absorption of hydrogen sulfide. The activity of soda lime is only for removing moisture and carbon dioxide in air.

This experiment showed that the absorption of hydrogen sulfide is concerned to Lewatit TP 208.

Determination of required amount of Lewatit TP 208 for removal of hydrogen sulfide in air of submarine: The amount of hydrogen sulfide produced in this experiment was 0.194 g and the absorbent used 30 g Lewatit TP 208.

The air volume of classical submarine is approximately 710 m^3. Threshold value (THV) of hydrogen sulfide is 10 µg/L. As indicated above: 30 g Lewatit TP 208 can remove 0.194 g hydrogen sulfide. The required amount of Lewatit TP 208 for the air volume of submarine calculated from threshold value of hydrogen sulfide. Finally, required amount of Lewatit TP 208 was 11 kg.

Soda lime cartilage (Drager) is commonly used in submarine for the remove of moisture and carbon dioxide in air. In proposal technique soda lime can be combined with Lewatit TP 208 in the same cartilage. This technique is easy and can be applicable for removal of two inconvenient in air of submarine. The change of cartilage can be arranged after the hydrogen sulfide control in air of submarine.

The other experimental technique, lead acetate and zinc acetate gave also best results but there are not practical for application in submarine.

Aeration of air in submarine is very important point for health of submariner. The change of proposed cartilage can be arranged after the hydrogen sulfide control in air of submarine.

This is first record on the removal of hydrogen sulfide in air of submarine by Lewatit TP 208.

Özet

Bu çalışmada, denizaltı havasında hidrojen sülfitin giderilmesi için bir metot önerilmiştir. Bunun için Lewatit TP 208 kullanılmıştır. Yapılan deneyde sülfürik asit ile potasyum sülfit ile reaksiyon sonucu oluşan hidrojen sülfitin Lewatit TP 208 ve soda lime içeren kolondan geçirilmesi sonucu hidrojen sülfitin tutulduğu ispatlanmıştır. Bu şekilde denizaltında halen uygulanan 5 kiloluk soda lime (Drager) kartilajının yerine aynı hacimde fakat soda lime ve Lewatit TP 208'i raflar içinde içeren Drager soda lime kartilajına benzer Şekil 2'de görüldüğü gibi bir düzen önerilmiştir. Önerilen bu teklif ile deniz altı havasında mevcut hidrojen sülfit ve rutubetin aynı zamanda giderilmesi mümkündür. Bu şekilde denizaltının ortalama hacmi olan 710 m^3 hava için gerekli lewatit miktarı 11 kg olarak hesaplanmıştır. Bu denizaltı havasındaki hidrojen sülfitin giderilmesi için önerilen bu teknik literatürde ilktir.

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