Technology of Water Purification from Hydrogen Sulphide and Its Utilization

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Abstract. The article discussed a technology for cleaning natural reservoirs from hydrogen sulphide to improve the environment. The choice of research methods was to organize the creation of an airlift due to the electrolysis of seawater. To purify seawater from hydrogen sulphide, electrolysis with the release of hydrogen and oxygen is used. The released gases create an airlift effect, due to which the hydrogen sulphide rises to the surface, where it is captured for further separation. By-products of the electrolysis of seawater, chlorine and sodium, due to their good solubility in water, are converted into alkali and acid and, as a result of the neutralization reaction, return to the reservoir. The paper also discusses the features of the electrolysis of seawater. The use of the proposed approach will improve the ecological situation and, in particular, will lead to an increase in fish stocks and in the restoration of the red algae population.

1. Introduction

Hydrogen sulfide in the Black Sea was discovered in the late 19th century. And since then, there have been extensive discussions about its possible use. On the one hand, hydrogen sulfide is a renewable potential source of energy and sulfur. But, on the other hand, there is an environmental problem with the rise of hydrogen sulfide in the surface sea layers [1]. The hydrogen sulfide zone begins at depths of 150-200 meters with a gradual increase in the concentration to 13-14 ml/l [2]. But the relative concentration of hydrogen sulfide is small, which causes problems with the profitability of its production from large volumes of water with simultaneous purification from impurities. The concentration of hydrogen sulfide is a fraction of a percent relative to its saturated solution.

Thus, the development and justification of cost-effective technologies for the use of hydrogen sulfide is currently relevant [3-5].

2. The technology of seawater purification from hydrogen sulfide on the basis of an aerolift

At various times, a number of approaches using airlift have been considered. In the early 90's, Ilya Varshavsky considered a technology in which it was supposed to create an airlift from hydrogen bubbles produced by the chemical reaction of activated aluminium with seawater. The hydrogen, rising up through the pipe, carried up the water along with the hydrogen sulphide dissolved in it. From the suspension moving to the surface of the water, due to the pressure drop, dissolved hydrogen sulphide began to be released, which enhanced the effect of the air lift. This technology used activated aluminium based on an alloy of aluminium with indium and gallium. Such an alloy successfully releases hydrogen...
from water, while indium and gallium are irretrievably consumed, which is economically unprofitable, since these components are close to gold in cost.

As an alternative, instead of indium and gallium, it is proposed to use an aluminium alloy with a few percent of copper, for example, 5-8% [6,7], or to use the alloy D16 (duralumin), which also contains copper. These alloys are well established as a cathode material in the electrolysis of water to produce hydrogen. In the proposed method, it is cheaper to organize an airlift using the decomposition of water by electrolysis. This work and experiments were conducted at the Mechanical Engineering Research Institute of the Russian Academy of Sciences.

Figure 1 shows a diagram of a device that implements the proposed technology. The pipe is made of a light aluminium alloy AMG-6, almost not subject to corrosion in seawater.

The pipe in this case is the anode, and the cathode is a round solid cylinder made of aluminium alloy located in the center. The lower end of the pipe is closed, and water with dissolved hydrogen sulphide enters through the side water intakes, which involves moving the pipe with the help of a vessel, i.e., water purification from hydrogen sulphide occurs in a decent water area. The closed lower part of the pipe involves the collection of electrochemical reaction products that are heavier than water and are not soluble in water.

The advantage of this method is that this process will be regulated by changing the power of electricity supplied from a constant current source to the anode-cathode circuit. Unlike the technical solution [7], it will not be necessary to use a pump to organize the initial movement of water with hydrogen sulphide dissolved in it up to the surface of the reservoir. This is done by applying a large amount of power to the electrolysis cell at the beginning.

Figure 1. Scheme of the installation for the purification of seawater from hydrogen sulphide.
3. Electrolysis of seawater

It should be noted that the electrolysis of seawater with hydrogen sulfide dissolved in it is somewhat different from the electrolysis of ordinary water. Seawater contains mainly sodium chloride, i.e. sodium cations and chlorine anions and water molecules. Therefore, along with hydrogen, sodium will be released at the cathode. Sodium with water molecules forms NaOH + H₂, which on the one hand gives water softening (which is useful in small amounts), and on the other hand increases electrolysis, which saves electricity. The additional hydrogen from this chemical reaction further enhances the airlift.

At the anode, along with oxygen, chlorine is released, which is well dissolved in water to form HCl

\[ 2\text{Cl} + \text{H}_2\text{O} + 2\text{HCl} + 0,5\text{O}_2 \]  

(1)

and combining with NaOH gives a neutralization reaction

\[ \text{NaOH} + \text{HCl} = \text{NaCl} + \text{H}_2\text{O} \]  

(2)

Oxygen, slightly dissolved in water, is involved in increasing the process of airlift and there is also aeration of hydrogen sulfide and its chemical oxidation with oxygen, which can occur in the receiver.

Below are the various chemical reactions of the resulting hydrogen sulphide: when there is a lack of oxygen, for example, in the receiver:

\[ 2\text{H}_2\text{S} + \text{O}_2 = 2\text{S} + 2\text{H}_2\text{O} \]  

(3)

An industrial method for producing sulfur is based on this reaction. In this case, only sulfur is synthesized and hydrogen is not used as fuel. For the production of both sulfur and hydrogen, the solution is given below.

If hydrogen sulfide is simply burned as fuel to produce heat, then in the air containing oxygen, hydrogen sulfide burns with a blue-tinged flame.

\[ 2\text{H}_2\text{S} + 3\text{O}_2 = 2\text{H}_2\text{O} + 2\text{SO}_2 \]  

(4)

Hydrogen sulfide reacts with alkalis:

\[ \text{H}_2\text{S} + 2\text{NaOH} = \text{Na}_2\text{S} + 2\text{H}_2\text{O} \]  

(5)

Hydrogen sulfide reacts with alkalis:

\[ \text{H}_2\text{S} + \text{NaOH} = \text{NaHS} + \text{H}_2\text{O} \]  

(6)

Hydrogen sulfide also reacts with many other oxidizing agents, and when it is oxidized in solutions, free sulfur or the SO42-ion is formed, for example:

\[ 3\text{H}_2\text{S} + 4\text{HClO}_3 = 3\text{H}_2\text{SO}_4 + 4\text{HCl} \]  

(7)

\[ 2\text{H}_2\text{S} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{S} \]  

(8)

In the receiver, hydrogen sulfide is separated from water. The water flows into the reservoir, and the hydrogen sulfide compressor is fed to the electrolyzer, where it is first liquefied, and then decomposed into hydrogen and sulfur. The resulting hydrogen is partly used to generate the energy needed to compress and decompose hydrogen sulfide, and partly as an environmentally friendly fuel.

Sulfur is used in various sectors of the national economy. Sulfur is used in electronic technology, in the manufacture of optical devices, phosphors, in the production of pharmaceutical and cosmetic products — lotions, ointments, remedies for skin diseases. Half of the sulfur produced is used in the production of sulfuric acid.

Sulfur is used for the vulcanization of rubber, as a fungicide in agriculture and as colloidal sulfur-a drug. Also, sulfur in the composition of serobitum compositions is used for the production of sulfur asphalt, and as a substitute for Portland cement - for the production of sulfur concrete. Sulfur is used for the production of pyrotechnic compositions, previously used in the production of gunpowder, used for the production of matches.

The annual global consumption of hydrogen exceeds 1 million tons. The use of hydrogen is diverse:
• In the chemical industry, it serves as a raw material for the production of many very important products (ammonia, etc.). It is also used in the production of such a large-capacity chemical substance as aniline. Hydrogen is used in the synthesis of ammonia and for the production of hydrochloric acid.
• In the food industry - for the production of solid fats from vegetable oils, etc. The high temperature (up to 2600°C) obtained by hydrogen in oxygen is used for melting refractory metals, quartz, etc.
• In rocket science, liquid hydrogen is one of the most efficient jet fuels.
• In petrochemicals, it is used to hydrogenate hydrocarbons from chemically bound sulfur.
• Hydrocracking (cracking in a hydrogen atmosphere) of natural hydrocarbons produces high-octane gasoline. As a reducing agent, hydrogen is used in the production of some particularly pure metals, catalysts.
• In analytical chemistry, hydrogen sulfide and hydrogen sulfide water are used as reagents for the precipitation of heavy metals, whose sulfides are very slightly soluble.
• In medicine - in the composition of natural and artificial hydrogen sulfide baths, as well as in the composition of some mineral waters.
• Hydrogen sulfide is used to produce sulfuric acid, elemental sulfur, and sulfides.
• Used in organic synthesis to produce thiophene and mercaptans.

4. Estimated calculations

It is known that the area of the Black Sea is \( S=420.3 \text{ thousand km}^2 \). The maximum depth is 2210 m. The depth from the surface of the sea free of hydrogen sulfide is on average 160 m. Assuming that the shape of the Black Sea bath will be the average between the cone and the cylinder, we assume that the volume of water \( V \) with hydrogen sulfide is equal to:

\[
V = \frac{2}{3}S(H - a) = \frac{2}{3} \times 420,3 \times 2050 \times 10^6 = 575 \times 10^9 \text{ m}^3 \quad (9)
\]

It is known that the hydrogen sulphide layer of the Black Sea water contains an average of 13 g / m\(^3\) of hydrogen sulphide, then the mass of hydrogen sulphide \( M_{sv} \) will be

\[
M_{sv} = 0.013 \times 575 \times 10^9 = 7,5 \times 10^9 \text{ kg} \quad (10)
\]

Hydrogen occupies 1/17th part of hydrogen sulphide, so from this hydrogen sulphide you can get hydrogen \( 4.4 \times 10^8 \text{ kg} \), and sulfur, respectively, \( 70.4 \times 10^8 \text{ kg} \).

When burning \( 4.4 \times 10^8 \text{ kg} \) of hydrogen, you can get \( 16,86 \times 10^9 \text{ kWh} \) energy. If we take into account the efficiency of fuel cells of 0.5, then when converted to electricity, we get \( 8,43 \times 10^9 \text{ kWh} \) — this is 1.5 times more than the annual electricity consumption of Moscow.

Theoretically, the decomposition of hydrogen sulfide into hydrogen and sulfur consumes 12 times less energy than is obtained by burning hydrogen. As an alternative, you can use the plasma-membrane technology reactor of the Institute of Hydrogen Energy and Plasma Technology of the Kurchatov Center, which consumes 1 kw-hour of electricity to produce 1 cubic meter of hydrogen and 1.4 kg of sulfur.

5. Conclusion

The paper proposes a technology for cleaning natural reservoirs from hydrogen sulfide to improve the environment. The technology is based on the organization of the creation of an airlift due to the electrolysis of seawater. It is shown that electrolysis can be used to purify seawater from hydrogen sulfide. As a result of electrolysis, hydrogen is released at the cathode, and oxygen is released at the anode. Both gases create the effect of an aerolift, due to which hydrogen sulfide rises to the surface of the reservoir, where it is captured for further separation.

By-products of the electrolysis of seawater, chlorine and sodium, due to their good solubility in water, are converted into alkali and acid and, as a result of the neutralization reaction, return to the reservoir. The use of the proposed approach will improve the ecological situation and, in particular, will lead to an increase in fish stocks and in the restoration of the population of red algae, in particular, in the Black Sea near the Crimean coast.
6. References

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