Comparison of sulfine hydrogen cleaning processes in a gas mixture in a packed adsorprial and electrochemical reactors

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Abstract. In this article given a comparative economic and environmental calculation of the use of a packed absorption column and an electrochemical reactor designed to purify air of hydrogen sulfide in the processes of ensuring environmental safety from potentially negative impacts of the surrounding technical facilities of the city, accompanied by emissions of hydrogen sulfide generated in sewers and emitted into the air of settlements. A significant advantage of the electrochemical air purification from hydrogen sulfide is shown compared with the absorption method of cleaning in packed columns using an aqueous solution of monoethanolamine as an absorbent. On the basis of practical experimental data, the optimal technological parameters of the process of electrochemical oxidation of hydrogen sulfide (current and voltage values) and the circuit diagram of a flow-through electrochemical reactor are determined.

1. Introduction
The problem of cleaning a gas mixture from hydrogen sulfide is relevant, because hydrogen sulfide is an environmentally hazardous substance [1]. The problem of hydrogen sulfide in the urban environment is becoming acute since an increase in living standards, an increase in the use of vehicles by the population, leads to a change in the concentration characteristics of the air environment of the city. Sewerage systems of the city experience an increase in load every year. This factor, together with the temporary degradation of sewer networks, leads to an increase in accidental emissions of their gas contents. One of the main agents that violate the qualitative characteristics of the material of sewer pipes (concrete) is hydrogen sulfide, which is formed as a result of the life of the microflora of sewer systems. The resulting hydrogen sulfide actively interacts with the pipe material, translating them into a less stable state. This creates the conditions for the emergency release of hydrogen sulfide into the surrounding space of the urban environment. In the area of emissions, in the working area of sewage treatment plants providing waste processing, a hazardous zone arises for humans. All this creates the problem of combating hydrogen sulfide with the involvement of various methods for cleaning gas environments from hydrogen sulfide. Traditional industrial methods for purifying air and gases from H₂S are based on the use of iron compounds [2] that bind the sulfide ion to the solid phase, dosing of nitrates and nitrites [3,4], which kill the microflora of sewer pipes, magnesium hydroxides [5], calcium nitrates [6] and nitrate nitrogen [7], chemically linking the sulfide ion with its transition to the salt state. These methods lead to the formation of products requiring further disposal, which further increases the environmental burden on the environment.
From all the physicochemical processes, the most industrially used method is based on mass transfer sorption processes [8]. However, this method has a multi-stage structure and the process of utilizing the separated hydrogen sulfide leads to the formation of an equally environmentally problematic product - gaseous sulfur oxides. Electrochemical methods [9, 10] for the oxidation of hydrogen sulfide are very promising, where the end products are ecologically pure sulfur and gaseous hydrogen. In this regard, the question arises of comparing the qualitative and economic aspects of using the above methods [11].

Below are the initial calculation data results of the absorption column, in which the gases generated in the sewers are cleaned of hydrogen sulfide and calculations using the electrochemical oxidation method. An aqueous solution of monoethanolamine [12], as the most commonly used in absorption processes, is used as an absorbent. For the calculation, the initial data were used [13, 14]: Henry's constant $E = 3760 \text{ mmHg}$; Raschig rings size 8x8x12 [13]; specific surface area $\sigma = 570 \text{ m}^2/\text{m}^3$; free volume $\varepsilon = 0,64 \text{ m}^3/\text{m}^3$; solution density $\rho_\text{e} = 1027 \text{ kg/m}^3$; solution viscosity $\mu_\text{e} = 1.43 \cdot 10^{-3} \text{ Pa}\cdot\text{s}$; gas viscosity at $25^\circ\text{C} \mu_\text{e} = 1.43 \cdot 10^{-3} \text{ Pa}\cdot\text{s}$; column pressure $P_\text{a} = 1.033 \text{ atm}$; the initial concentration of $\text{H}_2\text{S}$ in the gas $C_\text{i} = 0.2 \text{ mg/m}^3$; final concentration of $\text{H}_2\text{S}$ in the gas (MPC) $C_\text{k} = 0.008 \text{ mg/m}^3$.

To perform calculations on the use of adsorption columns, the initial data were taken: column diameter $D = 80 \text{ mm}$; nozzle height $H = 813 \text{ mm}$; absorbent consumption (monoethanolamine) $L = 44.7 \text{ kg/h}$; the volume of the nozzle in the absorption column $V_\text{n} = 4.1 \text{ l}$; nozzle mass $m_\text{n} = 24.6 \text{ kg}$. From these data, at a temperature of $25^\circ\text{C}$, a productivity of $10 \text{ m}^3/\text{h}$ and a pressure of $1 \text{ atm.}$ In the range of the change in the initial concentration of hydrogen sulfide $C_\text{i} = 0.2 \text{ mg/m}^3$ to the final $C_\text{k} = 0.008 \text{ mg/m}^3$ [15], which corresponds to the maximum permissible concentration for hydrogen sulfide, the adsorber diameter should be $D = 80 \text{ mm}$, and the nozzle height - Raschig rings $H = 813 \text{ mm}$. That is, the dimensions of the nozzle of the absorption column are small, but its operation requires a continuous supply of adsorbent $L = 45 \text{ kg/h}$ and its regeneration, although each kilogram of absorbent captures only $0.043 \text{ mg}$ of $\text{H}_2\text{S}$ [12]. As a result, the annual consumption of absorbent will be $G_\text{L} = (24 \cdot 365) \cdot 45 = 394200 \text{ kg/h}$. With the cost of regeneration of $1 \text{ kg}$ of absorbent 2.3 rub/kg of the total annual costs for this operation are: $C_\text{L} = G_\text{L} \cdot 2.3 = 906.6 \text{ thousand rub/year.}$

The purpose of this work is to show, in comparative calculations, the advantages of the electrochemical process of cleaning the gases generated in sewers from hydrogen sulfide and a typical absorption process in a packed column.

At the Department of General and Applied Chemistry, IA&S Volgograd STU, an electrochemical method for purifying air from hydrogen sulfide has been developed, which allows locally, in the zone of hydrogen sulfide emission, to neutralize it with the release of environmentally friendly products: chemically pure sulfur and hydrogen [16]. Under laboratory conditions, in an experimental setup, air with hydrogen sulfide was purged through the tube at a speed of $V = 1 \text{ cm/s}$. Anode was installed inside the tube and its body was grounded (Fig. 1). The approximation of experimental data on the kinetics of the electrochemical decomposition of hydrogen sulfide to elemental sulfur can be described by the zero-order velocity equation

$$V_{\text{HS}} = \frac{dc}{d\tau} = \text{const}$$

(1)

with $t = 20^\circ\text{C}$

$$V_{\text{HS}} = 1.4 \text{ mg/m}^3\text{h}.$$  

Then the integral equation of this reaction at low concentration $C < 0.5 \text{ mg/m}^3$

$$c = c_0 - V_{\text{HS}} \cdot \tau$$

(2)

and the reaction time is determined by the equation:

$$\tau = \frac{c_0 - c_1}{V_{\text{HS}}}.$$  

(3)

We recalculate the reaction rate obtained in laboratory conditions for sulfur (formula 2) in the reaction rate for hydrogen sulfide:
\[ V_{W,S} = V_b \left( \frac{M_{W,S}}{M_S} \right) = 1.4 \cdot \frac{34}{32} = 1.5 \text{mg/m}^3\text{h} \] (4)

Was taken the initial concentration of hydrogen sulfide in the air formed at the exit of the collectors (city sewer wells) \( C_0 = 0.2 \text{ mg / m}^3 \), which is 25 times more than the permissible MPC, but 50 times less than the permissible in the working zone \( C_{0,w,z} = 10 \text{ mg/m}^3 \) [15]. Was measured maximum concentrations of \( \text{H}_2\text{S} \) in the reservoirs of various regions of Volgograd and Volzhsky [17].

The calculations according to equation (3) allow us to determine the average residence time of the cleaned air in an electrochemical reactor:

\[ \tau = \frac{C_0 - C_k}{0.008} = 0.135 \text{ of an hour} \] (5)

Carried out calculations of an electrochemical reactor for the same capacity for cleaned air \( q_v = 10 \text{ m}^3/\text{h} \) with the same initial and final concentrations of hydrogen sulfide. At an air speed of \( V = 1 \text{ cm/s} \), corresponding to its value in a laboratory setup, the cross-sectional area of an electrochemical reactor is determined by the continuity equation:

\[ S = \frac{q_v}{\omega} = \frac{1}{0.01 \cdot 3600} = 0.0278 \text{ m}^2, \] (6)

and case diameter

\[ d_s = \sqrt{\frac{4S}{\pi}} = \sqrt{\frac{0.0278}{0.785}} = 0.47 \text{ m}. \] (7)

Module volume taking into account (5)

\[ V = q_v \cdot \tau = 1 \cdot 0.135 = 0.135 \text{ m}^3. \] (8)

Then the length of the electrochemical reactor will be

\[ l = \frac{V}{S} = \frac{0.135}{0.0278} = 4.85 \text{ m}. \] (9)

The scheme of the calculated electrochemical reactor for a given capacity, initial and final concentration of \( \text{H}_2\text{S} \) is shown on Figure 1.

\[ q_v \rightarrow \text{C}_0 \rightarrow \text{anode} \rightarrow \text{cathode} \rightarrow q_v \rightarrow \text{C}_k \]

**Figure 1.** Diagram of an electrochemical reactor: \( \text{C}_0 \) – concentration of \( \text{H}_2\text{S} \) at the entrance, \( \text{C}_k \) – concentration at the exit \( \text{H}_2\text{S} \)

When the anode current density \( i = 0.8 \text{ A/m}^2 \) and voltage \( U = 2.5 \text{ V} \), corresponding to these parameters [18] in laboratory conditions, the surface of the anode will be:

\[ S_a = \pi \cdot d_a \cdot L = 3.14 \cdot 0.05 \cdot 121.25 = 19 \text{ dm}^2, \] where \( L = 2.5 \cdot 1 = 2.5 \cdot 4.85 = 21.25 \text{dm}^2 \) - anode length; \( d_a = 0.05 \text{ dm} \) - anode diameter.

In this case, the current in the electrochemical reactor [19]: \( I = S_a \cdot i_a = 19 \cdot 0.8 = 15.2 \text{ A} \), and power:

\[ N = J \cdot U = 15.2 \cdot 2.5 = 38 \text{ Vt} \]

The annual energy consumption in this case will be:
\[ E = \frac{24 \cdot 365 \cdot N}{1000} = 333 \text{ kW-h} \]

and its cost per year

\[ C_E = C_e \cdot E = 4.3 \cdot 333 = 1432 \text{ rub/year}, \]

where \( C_e = 4.3 \text{ rub/kW-h} \) – the cost of one kW-hour of electricity.

Thus, although the volume of the electrochemical reactor is \( V = 1.35 \text{ m}^3 \) compared with the volume of the absorber \( V = 0.0041 \text{ m}^3 \) when using it, the cost of electricity is 330 times less than the cost on the regeneration of the absorber. Along with this, it should be noted the technological flexibility of using the electrochemical method and the possibility of automation the cleaning and control of local hydrogen sulfide emissions, increasing the economic characteristics and, as a result, the environmental characteristics of the processes of protecting the urban environment from the effects of hydrogen sulfide emissions [20].

Table 1. The results of the absorption of hydrogen sulfide in air from a source of pollution by the proposed method.

| Hydrogen sulfide concentration, mg/m³ | 1   | 2   | 3   | 4   | 5   | 6   | 7   |
|-------------------------------------|-----|-----|-----|-----|-----|-----|-----|
| Before cleaning                     | 8.78| 9.20| 12.40|10.72|13.61|12.02|13.22|
| After cleaning                      | 0.01| 0.01| 0.01| 0.01| 0.02| 0.01| 0.02|
| The percentage of cleaning          | 99.88| 99.89| 99.92| 99.91| 99.97| 99.92| 99.85|

Table 1 shows data on the degree of gas purification from hydrogen sulfide at a sewage pumping station in Volgograd using a breadboard plant using the electrochemical method (16).

2. Summary
The above data of a comparative analysis of the methods of adsorption and electrochemical extraction and oxidation of hydrogen sulfide, in order to improve the ecological state of the environment, shows that the use of the electrochemical method allows efficient, without the formation of environmentally hazardous products, purification of a gases mixture from hydrogen sulfide. This technique can be recommended for use in gas mixture purification systems in various enterprises that have problems with the release of hydrogen sulfide during work.

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