

This paper reports a study into the influence of sodium carbonate concentration (10, 30, and 50 kg/m³) in the simultaneous presence of sodium thiosulfate (250 kg/m³) and quinhydrone (5 kg/m³) on the coefficient of the phase distribution of hydrogen sulfide in a quinhydrone absorbing solution. The research was carried out at the laboratory installation using chemical analysis methods of liquid and gas phases. It has been found that the coefficient of phase distribution increases dramatically with an increase in the degree of saturation of the quinhydrone solution with hydrogen sulfide. At the same time, in the presence of sodium thiosulfate in quinhydrone absorbing solutions, the coefficient of phase distribution increases compared to carbonate solutions of the same concentration. Thus, the partial hydrogen sulfide pressure over a quinhydrone solution at low degrees of hydrogen sulfide saturation (up to 3 %) is 5...10 times larger than that over soda solution, while at high degrees (60...80 %) it is almost the same. It can be argued that at the high concentrations of sodium carbonate and the degree of the saturation of quinhydrone solution with hydrogen sulfide the effect of sodium thiosulfate on the partial pressure of hydrogen sulfide decreases. An equation of the effect exerted by the NaHS concentration and the starting Na₂CO₃ concentration on the H₂S partial pressure over quinhydrone solutions has been proposed. Based on the experimental studies' results, the equilibrium constant values for a hydrogen sulfide chemisorption reaction involving a quinhydrone solution have been calculated. To ensure the high absorption capacity, the process of hydrogen sulfide chemisorption should be carried out using solutions with a maximum concentration of sodium carbonate, 40...50 kg/m³. The presence of ballast components (Na₂S₂O₃, NaHCO₃) slightly reduces the sorption capacity of an absorbing solution. The results obtained could be used in engineering calculations and when developing technology for purification of fuel gases from hydrogen sulfide by a quinhydrone method

Keywords: hydrogen sulfide, gas cleaning, chemisorption, quinhydrone method, absorbent solution, phase equilibrium

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INVESTIGATING EQUILIBRIUM IN THE SYSTEM OF A HYDROGEN SULFIDE-QUINHYDRONE ABSORBING SOLUTION

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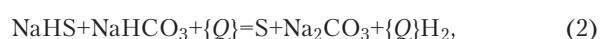
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1. Introduction

Purification of gases from hydrogen sulfide is an important and necessary process in gas production, oil refining, and coke-chemical industries [1–3]. The relevance of these processes is predetermined by the global development and application of biogas and biomethane technologies [4–7] and mass-exchange equipment of different types for gas purification [7–9].

The quinhydrone method of gas purification from hydrogen sulfide makes it possible to effectively clean both oxygen-containing (for example, ventilation) and oxygen-free fuel (natural, associated petroleum, etc.) gases. This method refers to the liquid-phase-oxidative ones [2–4] and can be described by the following basic reactions:



where {Q} and {Q}H₂ are the oxidative and reducing state of the quinhydrone oxidant [1], respectively.

Absorbing hydrogen sulfide from gases involves an absorbing solution that includes water, sodium carbonate, sodium hydrogen carbonate, sodium thiosulfate, quinhydrone oxidant, and dissolved oxygen [4, 10]. Sodium hydrogen carbonate forms from reaction (1), as well as a result of Na₂CO₃ interaction with carbon dioxide, which is often a component of fuel gases



Dissolved oxygen may be contained in the absorbing solution after the stage of its regeneration by air oxygen in line with reaction (3). Oxygen in the solution also causes an adverse reaction of the formation of sodium thiosulfate



Sodium thiosulphate, like other compounds, accumulates in the absorbing solution and affects its sorption properties [2, 4]. The absorbing solution must contain no more than 200...250 kg/m³ of Na₂S₂O₃ [2, 4, 10].

Reactions (1) to (3) during the purification of oxygen-containing gases from hydrogen sulfide proceed simultaneously in one device. This is facilitated by the high rates of oxidation of chemisorbed hydrogen sulfide by the quinhydrone oxidant and the regeneration of it by oxygen from the air [5], as well as the use of a high-intensity mass-exchange apparatus – the horizontal apparatus with bucket-like dispersers [11]. In the case of purifying oxygen-containing gases, the equilibrium distribution of hydrogen sulfide in the absorbing solution is not essential, because, due to the rapid course of reactions (2) and (3), the concentration of chemisorbed hydrogen sulfide in a quinhydrone solution is negligible. That does not require using the high concentrations of Na₂CO₃ in the solution (above 10 kg/m³).

During the purification of oxygen-free gases, the interaction by equation (1) should be carried out in an absorber; the reactions by equations (2) and (3) – in a solution regenerator. In this case, the equilibrium distribution of hydrogen sulfide in the absorbing solution has a decisive effect on the degree of gas purification in the absorber. At an average quinhydrone oxidant content in an absorbing solution of 5 kg/m³, the concentration of the chemisorbed hydrogen sulfide in the solution is significant [10].

In order to achieve the high efficiency of oxygen-free gases' purification from hydrogen sulfide using the quinhydrone method and to calculate the basic technological hardware for these processes, it is necessary to have data on the equilibrium distribution of hydrogen sulfide in a quinhydrone absorbing solution. In addition, it is necessary to ensure a high sorption capacity of this solution in terms of hydrogen sulfide to reduce the volume of circulation flows in the treatment system [2, 4].

2. Literature review and problem statement

Many studies have investigated the equilibrium concentrations of hydrogen sulfide in the systems gas-liquid using both physical solvents and solutions in which chemisorption processes take place.

Paper [12] reports data on the steam-liquid equilibrium for the binary system H₂S – H₂O in the temperature range of 298... 338 K for a pressure up to 4 MPa. The research was aimed at addressing issues related to condensed water formation to reduce the risk of hydrate formation, ice formation, corrosion, and two-phase flow problems in hydrogen sulfide-containing gas treatment facilities saturated with water vapor. Work [13] suggested a state equation (of the phase equilibrium) for the H₂S–H₂O system in a NaCl aqueous solution. The phase behavior of acidic gases CO₂ and H₂S in salt systems is essential for the geological storage of greenhouse gases, acidic gas emissions, and increased oil production [14]. For a similar purpose, studies of hydrogen sulfide solubility in aqueous solutions of single salts of sodium sulfate, ammonium sulfate, sodium chloride, and ammonium chloride were carried out at temperatures from 313 to 393 K and a total

pressure of up to 10 MPa [15]. It was noted that at the high concentrations of hydrogen sulfide there is a second liquid phase, enriched with hydrogen sulfide, similar to salt-free systems. The above processes, as well as the dissolution of H₂S in certain carbonate solvents (propylene carbonate, dimethyl carbonate, etc.) [16], occur according to the mechanism of physical dissolution.

Under industrial conditions, chemisorption processes are often used to remove acidic gases from gas flows. These processes are associated with the interaction of dissolved gas with the active component of the absorbing solution [17]. Paper [18] describes the equilibrium in the system of acidic gases-water-alkanolamines using thermodynamic calculations and taking into consideration the ionic uneven chemical reactions and processes of mass- and heat transfer. In addition, with the help of experimental research, hydrogen sulfide absorption by various aqueous and non-water solutions of amines (mono ethylene glycol, triethylene glycol, etc.) was studied [19, 20].

Thorough studies of equilibrium conditions in the system hydrogen sulfide– carbonate absorbing solution were carried out during the development and improvement of a vacuum carbonate method of purification of coke oven gas from hydrogen sulfide. In a state of equilibrium between the partial pressure of hydrogen sulfide in the gas phase and its concentration in the liquid phase, a certain ratio is established, which is characterized by the coefficient of phase distribution *m* (a phase equilibrium constant). This quantity is equal to the ratio of the concentration of hydrogen sulfide in the gas phase to its concentration in the liquid phase. In other words, the coefficient of phase distribution *m_{px}*, Pa, can be calculated from the following equation

$$m_{px} = \frac{p^*}{x}, \quad (6)$$

where *x* is the concentration of hydrogen sulfide in the liquid phase, molar units; *p*^{*} is the equilibrium partial pressure of hydrogen sulfide over the solution, Pa.

The coefficient of phase distribution depends on the pressure, temperature, and composition of the solution. The main factor influencing it is the temperature, with the increase in which the coefficient of phase distribution increases. Thus, for the system H₂S – H₂O, the phase distribution coefficient *m_{px}*(H₂O) at 20 °C is 490·10², at 30 °C – 617·10², at 40 °C – 755·10² kPa [21]. The above dependence holds for gases at their partial pressure of less than 0.1 MPa as *m_{px}* depends insignificantly on overall pressure if it is ≤0.5 MPa [21].

The coefficient of phase distribution in electrolyte solutions is mainly increasing due to the presence of additional substances that do not interact with dissolving gas. At the same time, in the interaction of this gas with the components of the absorbing solution, the gas partial pressure decreases while solubility increases, that is, *m* decreases [21].

In the system hydrogen sulfide–soda absorbing solution, there is a reaction of the hydrogen sulfide chemisorption by the solution in line with equation (1). The equilibrium of this reaction is determined by the constant of equilibrium *K*

$$K = \frac{[\text{HS}^-] \cdot [\text{HCO}_3^-]}{[\text{CO}_3^{2-}] \cdot [\text{H}_2\text{S}]}. \quad (7)$$

It is known that the equilibrium constant depends on the nature of reactive substances and temperature and does not

depend on the concentration of reactive substances, or rather their activities. The latter is true for non-high concentrations of reactive substances [21].

Paper [22] examined in detail the equilibrium in the system $\text{H}_2\text{S}-\text{Na}_2\text{CO}_3-\text{NaHCO}_3-\text{NaHS}-\text{H}_2\text{O}$. The dependence of the partial pressure of hydrogen sulfide (p , mmHg) over soda solution (1N Na_2CO_3) in the temperature interval (t) 20...60 °C was described by the following equation

$$p = 5.4 \cdot (t + 48) \cdot C^{3.04}, \quad (8)$$

where C is the concentration of hydrogen sulfide in solution, mol/dm³.

An equilibrium constant was determined for the reaction of hydrogen sulfide chemisorption by a carbonate solution from equation (1); an equation was derived to calculate its changes at different temperatures (T , K) [22]

$$\lg K = \frac{2,500}{4.57 \cdot T} - 3.16. \quad (9)$$

For the system hydrogen sulfide–sodium carbonate, the author of [22] calculated an equilibrium constant according to the isotherm equation, which, at a temperature of 298 K, is equal to 324, and, at 333 K, to 208 mol/(l·atm). It was shown that the calculations' results, based on two techniques, are adequate; for this system, an increase in temperature decreases the equilibrium constant K .

However, the empirical patterns of the system hydrogen sulfide–sodium carbonate describe only partially equilibrium systems. They cannot always be used for practical purposes in the presence of other components in the quinhydrone solution. The authors of [21] devised the procedures for calculating the influence of ballast components (the ionic capacity of these solutions) on a change in the distribution coefficient; however, at the high concentrations of components in solutions, such calculations become inadequate.

Therefore, studying the equilibrium distribution of the components in the multicomponent systems gas–liquid often involves experimental research. This approach is used in works [23–26], whose authors investigated the equilibrium concentrations of hydrogen sulfide in carbonate solutions in the presence of ballast substances (NaCNS , NaHCO_3 , NaCl , etc.). Studies of equilibrium in the vacuum-carbonate methods of gas purification from hydrogen sulfide showed that in the presence of ballast salts (NaCNS , NaHCO_3) in absorbing solutions, compared to pure soda solutions, the partial pressure of hydrogen sulfide above them increases [24, 25].

Study [26] investigated and calculated the phase equilibrium for the system coke gas–soda absorbing solution. The values of the reaction equilibrium constant (1) and the material balance of the absorber were used to calculate the values of the equilibrium pressure of hydrogen sulfide for the height of the absorber for gases that contained, g/m³: 18 H_2S , 42 CO_2 , and 1.5 HCN . Based on the calculations, the following equation was proposed

$$p = 12.3 \cdot C_{\text{H}_2\text{S}} + 17 \cdot (t + 48) \cdot C_{\text{H}_2\text{S}}^{3.04}, \quad (10)$$

which, at a temperature of 308 K, yielded convergent results with the values calculated from the equation for the equilibrium constant K . As indicated in [26], studying the effect of the concentration of ballast salts on equilibrium requires taking

into consideration the value of the equilibrium constant for the principal reaction at different compositions of the absorbing solution at the top and bottom of the column, that is, the degree of saturation of the absorbing solution with hydrogen sulfide.

It is obvious that in a quinhydrone absorbing solution the ballast substances would influence the equilibrium distribution of hydrogen sulfide. In the absorbing column, there would occur the sorption of hydrogen sulfide by the quinhydrone absorbing solution in line with equations (1), and, partially, the interaction in line with equation (2), which would affect the process equilibrium. The lack of data on the equilibrium distribution of hydrogen sulfide and the equilibrium constant for the reaction of hydrogen sulfide chemisorption in quinhydrone absorbing solutions indicates the expediency of experimental research to determine them.

3. The aim and objectives of the study

The aim of this study is to determine the coefficient of the phase distribution of hydrogen sulfide in quinhydrone absorbing solutions and the equilibrium constant for the H_2S chemisorption reaction. This would make it possible to use the obtained data for engineering calculations of mass-exchange equipment and the development of technologies for purifying fuel (oxygen-free) gases from hydrogen sulfide using a quinhydrone method.

To accomplish the aim, the following tasks have been set:

- to determine experimentally the partial pressure of hydrogen sulfide and calculate the value of the coefficient of phase equilibrium of the latter in quinhydrone absorbing solutions depending on the degree of their saturation with hydrogen sulfide;
- to derive the mathematical dependence of the partial pressure of hydrogen sulfide over quinhydrone solutions on its content in the solution and the starting concentration of sodium carbonate;
- to calculate, based on the results of experimental studies, the value of the equilibrium constant of the hydrogen sulfide chemisorption reaction involving quinhydrone absorbing solutions and interpret these data in terms of the sorption capacity of the solution.

4. Materials and methods to study the partial pressure of hydrogen sulfide over quinhydrone absorbing solutions

We studied the equilibrium concentrations of hydrogen sulfide in the system quinhydrone absorbing solution–hydrogen sulfide–inert gas (nitrogen) using a static method at the laboratory installation whose scheme is shown in Fig. 1.

The installation for examining the sorption equilibrium consisted of units that prepare the nitrogen-hydrogen sulfide gas mixture, saturate absorbing solution with hydrogen sulfide, and take the samples of gas and liquid for analysis.

We saturated the absorbing solution with hydrogen sulfide in a system of two conical flasks (10) and (13), equipped with bubblers and upper and lower nozzles. One of the flasks was placed stationary (Fig. 1, flask 10), and the other could be installed above or below the stationary one. First, we poured a quinhydrone absorbing solution into the upper flask. Next, the flasks were sealed and connected with hoses, as shown in the figure. Then we blew nitrogen from cylinder 9 through them to squeeze out the air.

We passed through the absorbing solution in the upper flask a certain amount of hydrogen sulfide, controlled by the rheometer and the sorption time of the gas mixture. Next, we manipulated the flasks. As the taps (K1) and (K2) were opened, the solution from the upper flask spilled into the lower one. Gas from the lower flask entered the released volume of this flask, which, at the same time, bubbled through the absorbing solution that remained in the upper one. After the solution flowed from the upper flask to the bottom one, the latter was raised to repeat the above activities until the pH value of the solution stabilized. After several control "rinsing" of the gas, the gas and liquid phases samples were selected for analysis on the hydrogen sulfide content. We selected the gas phase for analysis from the lower flask while the upper one, in the meantime, was replenished with nitrogen. During each sampling, the amount of hydrogen sulfide in the system decreased, allowing several more times to determine the equilibrium concentrations of hydrogen sulfide without replacing the liquid phase.

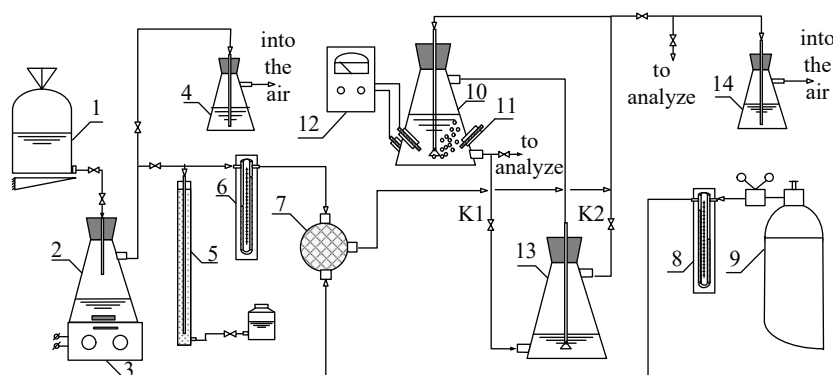


Fig. 1. Schematic of laboratory installation: 1 – pressure container with sulfate acid; 2 – flask with sodium sulfide solution; 3 – magnetic stirrer; 4, 14 – sanitary containers with the acidified solution of KMnO_4 ; 5 – monostate; 6, 8 – rheometers; 7 – mixer; 9 – cylinder with N_2 ; 10, 13 – flasks with absorbing solution; 11 – thermometer; 12 – pH-meter

We studied the equilibrium concentrations of hydrogen sulfide over quinhydrone absorbing solutions at the starting concentrations of Na_2CO_3 of 10, 30, and 50 kg/m^3 (94.34; 283.0; and 471.7 mol/m^3 , respectively). The remaining parameters were constant: temperature, 298 K; the content in solution, kg/m^3 : quinhydrone – 5, sodium thiosulphate – 250.

Hydrogen sulfide was obtained by dosing 20 % of the sulphate acid solution in a ~10 % solution of sodium sulfide. Quinhydrone absorbing solutions were prepared by dissolving the appropriate amounts of sodium carbonate and quinhydrone (molar ratio, 2:1) in distilled water. The received solutions were aged for 7 days with the air access and at periodic stirring [10]. After that, other components were added to the solution to achieve the appropriate concentrations. All the reagents were categorized as "chemically pure". The analysis of the gas and liquid phases was carried out by iodometric and chromatographic methods [27].

The concentration of H_2S in the solution (x , molar units) was calculated as the ratio of the amount of H_2S (mol) to the amount of H_2O (mol) in the quinhydrone absorbing solution (that is, the content of sodium carbonate, quinhydrone, and sodium thiosulphate in the solution was not taken into consideration). The saturation

degree of the solution (α , %) was calculated as the ratio of the amount of NaHS (mol) in the solution to the starting amount of Na_2CO_3 (mol). Based on the value of H_2S concentration in the gas phase, we calculated its equilibrium partial pressure over quinhydrone solutions (p^* , Pa). To calculate the partial pressure of hydrogen sulfide over carbonate solutions, we used the values of the equilibrium constant, according to [22]. The equilibrium constant K was calculated from equation (7).

5. Results of studying the equilibrium distribution of hydrogen sulfide in quinhydrone absorbing solutions

5.1. Determining the partial pressure of hydrogen sulfide in quinhydrone absorbing solutions

The dependences of the equilibrium content of hydrogen sulfide over quinhydrone solutions on the saturation degree of H_2S solution and the concentration of Na_2CO_3 in the solution are given in Table 1.

The analysis of the obtained results shows that, as expected, with an increase in the degree of saturation of the quinhydrone absorbing solution with hydrogen sulfide (Table 1, column 4), the equilibrium partial pressure of hydrogen sulfide increases (Table 1, column 5). For the very low degrees of saturation of the absorbing solution with hydrogen sulfide (0.2...1.0 %), the equilibrium partial pressure of H_2S over the solution does not exceed 0.2...0.3 Pa. This makes it possible to purify the gases from hydrogen sulfide using quinhydrone solutions until the sanitary norm is reached (20 mg/nm^3 , or $p^*=1.33$ Pa) even at atmospheric pressure. With the increase in gas pressure, the partial pressure of hydrogen sulfide in it would increase proportionally, which could increase the driving force of chemisorption.

5.2. Mathematical notation of the study of results

The dependence of the H_2S partial pressure on its content and the starting concentration of sodium carbonate in the studied quinhydrone solutions at 298 K in logarithmic coordinates is properly described by a linear dependence (Fig. 2). For ease of use, the results of our calculations were mathematically treated using a method of the least squares with the approximation of values by the linear and power functions; hence, the mathematical dependence (11). Equation (11) describes with the high probability of approximation ($R^2 \geq 0.98$) the dependence of the equilibrium H_2S partial pressure on NaHS concentration and the starting concentration of Na_2CO_3 within 80 to 500 mol/m^3 for the quinhydrone absorbing solutions whose degree of hydrogen sulfide saturation is 2...87 %.

$$\lg p^* = 1.51 \cdot \lg \frac{C_{\text{NaHS}}}{(C_{\text{Na}_2\text{CO}_3(\text{start.})} - C_{\text{NaHS}})} + 1.71 \cdot C_{\text{Na}_2\text{CO}_3(\text{start.})}^{0.8}, \quad (11)$$

where p^* is the H_2S partial pressure, Pa; C_{NaHS} is the concentration of dissolved hydrogen sulfide, mol/m^3 ; $C_{\text{Na}_2\text{CO}_3(\text{start.})}$ is the starting concentration of sodium carbonate, mol/m^3 .

Results of studying and calculating the phase equilibrium

Concentration in solution, C, mol/m ³		Molar share of H ₂ S in solution, ×10 ³	Saturation degree of H ₂ S solution, α, %	Equilibrium partial pressure of H ₂ S p*, Pa, over solutions:		Phase distribution coefficient, m _{px} , Pa	Ratio $\frac{m_{px}(H_2O)}{m_{px}}$	Equilibrium constant, K, $\frac{mol}{Pa \cdot m^3}$
Na ₂ CO ₃	NaHS			quinhydrone	soda [5]			
1	2	3	4	5	6	7	8	9
C(Na ₂ CO ₃) (start.)=10 kg/m ³								
94.34	0	0	0	0	–	–	–	–
92.87	1.47	0.03	1.56	0.3	0.065	10,000	4,900	0.078
91.40	2.94	0.06	3.12	1.3	0.26	21,667	2,262	0.073
76.69	17.65	0.36	18.70	35,0	11.28	97,222	504.0	0.116
55.22	39.12	0.80	41.46	295	77.0	368,750	133.9	0.094
35.52	58.22	1.21	62.34	1,013	270.6	844,167	58.0	0.094
26.10	68.24	1.40	72.33	1,593	495.5	1,134,860	43.2	0.102
16.10	78.24	1.61	82.90	2,466	1,056	1,531,677	32.0	0.112
8.16	86.18	1.77	91.35	4,345	2,527	2,454,802	20.0	0.154
C(Na ₂ CO ₃) (start.)=30 kg/m ³								
283.00	0	0	0	0	–	–	–	–
281.53	1.47	0.03	0.52	0.2	0.02	6,557	7,472	0.038
224.18	58.82	1.22	20.78	94,0	42.9	77,049	635.9	0.164
165.35	117.65	2.44	41.57	409	232.5	167,622	292.3	0.205
106.53	176.47	3.66	62.36	1,332	812.0	363,934	134.6	0.219
77.12	205.88	4.28	72.75	2,000	1,527	467,289	104.9	0.275
47.70	235.30	4.88	83.14	4662	3,224	955,327	51.3	0.249
18.30	264.70	5.49	93.53	11,330	10,639	2,063,752	23.7	0.338
C(Na ₂ CO ₃) (start.)=50 kg/m ³								
471.70	0	0	0	0	–	–	–	–
468.76	2.94	0.06	0.70	0.2	0.05	3,257	15,043	0.092
412.88	58.82	1.23	12.47	27.4	23.28	22,312	2,196	0.306
354.05	117.65	2.46	24.94	154	108.6	62,678	782.0	0.254
236.40	235.29	4.91	49.90	666	650.5	135,558	361.5	0.352
177.58	294.12	6.14	62.35	1332	1353	216,867	225.9	0.366
118.76	352.94	7.37	74.82	3,330	2,913	451,831	108.4	0.315
59.94	411.76	8.60	87.29	11,330	7,858	1,317,441	37.2	0.250
30.52	441.18	9.21	93.53	19,980	17,715	2,168,910	22.6	0.319

Table 1 factors influencing the kinetics of hydrogen sulfide chemisorption by quinhydrone absorbing solutions. Based on the results of our research, the coefficient of the phase distribution of hydrogen sulfide (Table 1, column 7) increases dramatically with the increase in the degree of it saturating the quinhydrone solution and decreases with the increase in the concentration of sodium carbonate in the solution. Thus, for a degree of the saturation of quinhydrone solution with hydrogen sulfide of 0.52 % and a concentration of Na₂CO₃ of 30 kg/m³, m_{px}=6,557 Pa; for the same degree of the solution saturation and at a soda concentration of 50 kg/m³, m_{px}=2,420 Pa; and for a saturation degree of 93.53 % and a soda concentration of 50 g/m³, m_{px}=2,168,910 Pa.

Based on the experimental data, we calculated the values of the reaction equilibrium constant (1). For the quinhydrone solution, depending on the degree of its saturation with hydrogen sulfide and the starting concentration of sodium carbonate, there are fluctuations in these values. Thus, the equilibrium constant, with an increase in the degree of the saturation of the solution with hydrogen sulfide from ~1 % to ~82 %, increases by 1.5...5 times, and, with an increase in the concentration of sodium carbonate in the absorbing solution from 10 to 50 kg/m³, K increases by ~1.5 times.

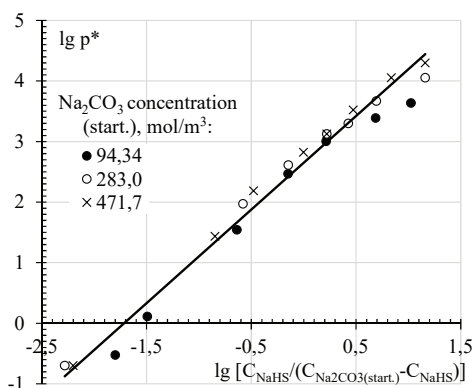


Fig. 2. Logarithmic dependence of H₂S partial pressure on the equilibrium NaHS concentration and the starting Na₂CO₃ concentration for quinhydrone absorbing solutions

5. 3. Calculation of the equilibrium constant for the hydrogen sulfide chemisorption reaction involving quinhydrone absorbing solutions

The coefficient of phase distribution and the equilibrium constant of chemical reaction (1) are among the important

6. Discussion of results of studying the equilibrium in the system hydrogen sulfide–quinhydrone absorbing solutions

The comparison of the H₂S equilibrium partial pressure values over the quinhydrone (Table 1, column 5) and soda solutions of the same concentration of Na₂CO₃ (Table 1, column 6) [22] shows that it is larger above the quinhydrone solution. At low degrees of hydrogen sulfide saturation (up to 3 %), the H₂S partial pressure over the quinhydrone solution is 5...10 times larger than that over the soda solution, and, at high degrees (60...80 %), it is greater only by 2...3 times at the starting concentration of Na₂CO₃ of 94.34 mol/m³ (10 kg/m³) and almost the same at the starting concentration of Na₂CO₃ of 471.7 mol/m³ (50 kg/m³) in solution. That is, at the high concentrations of sodium carbonate and the degree of saturation of the quinhydrone solution with hydrogen sulfide, the effect of sodium thiosulfate content on the partial pressure of hydrogen sulfide decreases.

Similar dependences were established in work [24]. In the presence of ballast salts in an absorbing solution with a concentration of 150...170 kg/m³ of NaCNS, the H₂S

pressure over an absorbing solution, compared to pure soda solution, increased by 2.7...4 times. However, the greater the concentration of hydrogen sulfide in the solution, the less the effect of the NaCNS concentration.

It is obvious that the derived results of the influence exerted on the coefficient of equilibrium distribution by hydrogen sulfide are associated with changes in the ionic capacity of solutions [23, 24] with the growth in the concentrations of components in the quinhydrone solution.

Column 8 in Table 1 gives the ratios of the phase hydrogen sulfide distribution coefficient in water m_{px} (H_2O) at 298 K [21] to our calculated hydrogen sulfide distribution coefficients in the quinhydrone solutions m_{px} . This ratio acquires a value of 5,000...15,000 for the low saturation degrees α and up to ~20 for high α (91...99%). Consequently, this clearly indicates the effect of the degree of the saturation of the solution with hydrogen sulfide and the need to use more complex engineering calculations than recommended in [21].

If one analyzes the operation of absorbing columns in the technologies of gas purification from hydrogen sulfide, the absorbing solutions with a low degree of saturation with hydrogen sulfide are present at the last stages of gas chemisorption (at the top of the column). Given that the partial pressure of hydrogen sulfide over carbonate solutions containing ballast components is greater than that over ballast-free carbonate solutions, for such solutions (with ballast components) the removal (passing) of H_2S is more likely.

Obviously, to reduce the influence of ballast salts on the purification of coke gas by a vacuum carbonate method, a two-stage scheme was proposed where stage I implies rough purification and stage II – fine cleaning. At the stage of fine cleaning, it is recommended to reduce the concentration of ballast salts from 250 to 50 kg/m³; then the equilibrium concentration of hydrogen sulfide over the solution decreases by 4 times while soda solubility increases by 2 times [25].

We calculated the process of natural gas purification at the Lokachinsky gas field (Volyn oblast, Ukraine) for the following initial data: gas consumption, 78,000 m³/day; starting hydrogen sulfide content is 1.6 kg/m³. To achieve the rated residual hydrogen sulfide content in the gas of 7 mg/m³, it is necessary to carry out the process of this gas purification at an efficiency of 99.56%. To ensure such deep gas purification, we have developed the technology of two-stage gas purification using a quinhydrone method [28]. It is known that it is necessary, in the cyclic liquid-phase oxidative processes of gas purification from hydrogen sulfide, to remove part of the solution from the cycle to prevent the accumulation of ballast components and to replace it with fresh (without ballast components) [1–3]. Therefore, according to the developed technology, the basic gas purification from hydrogen sulfide should be carried out with a regenerated absorbing solution; the post-purification – with a fresh solution while ensuring the balance of components in the solution. It is obvious that, at the stage of chemisorption

of hydrogen sulfide, it is necessary to feed an absorbing solution after its deep regeneration.

The increase in the estimated values of the reaction equilibrium constant (1) (Table 1, column 9) with the increase in the degree of the saturation of the solution with hydrogen sulfide and the starting concentration of sodium carbonate can obviously be explained by the drop in the activity of reactive substances with the growth of their concentrations.

The analysis of our study results also indicates that in order to ensure the high absorption capacity of the solution, the process of hydrogen sulfide chemisorption should be carried out using a quinhydrone solution with the maximum amount of sodium carbonate (40...50 kg/m³). Increasing gas pressure would contribute to shifting the balance of the reaction to the right. The presence of other (ballast) components in the solution, $Na_2S_2O_3$, $NaHCO_3$, would slightly reduce the sorption capacity of such an absorbing solution, affecting the shifting of the balance of the reaction (1) to the left. In this case, such physical-chemical indicators of the absorbing solution would increase as its viscosity and density; they adversely affect the rate of hydrogen sulfide chemisorption. In addition, the content of alkaline components affects the regeneration of the absorbing solution. Therefore, the optimal composition of the quinhydrone absorbing solution can be chosen only based on the results of studying both the kinetics of the processes of hydrogen sulfide chemisorption and the regeneration of the absorbing solution.

7. Conclusions

1. The partial pressure of hydrogen sulfide over quinhydrone solutions increases with an increase in the solution saturation with hydrogen sulfide. Due to the presence of additional components in the quinhydrone absorbing solution, the partial pressure of hydrogen sulfide over such a solution is greater compared to a pure soda solution. However, at the high concentrations of sodium carbonate in a quinhydrone solution, this increase in partial pressure does not become significant.

2. The dependence of the equilibrium H_2S partial pressure over quinhydrone absorbing solutions on the NaHS concentration and the starting Na_2CO_3 concentration is described by a linear dependence in logarithmic coordinates. The proposed equation is valid for the quinhydrone absorbing solutions with a starting concentration of sodium carbonate in the range of 80 to 500 mol/m³ and a degree of hydrogen sulfide saturation of 2...87%.

3. To ensure the high absorption capacity of the quinhydrone solution, the process of hydrogen sulfide chemisorption should involve the solutions with a maximum concentration of sodium carbonate (40...50 kg/m³). The presence of ballast components ($Na_2S_2O_3$, $NaHCO_3$) affects the equilibrium by slightly reducing the sorption capacity of the absorbing solution.

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