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STUDY OF OXYGEN CHEMISORPTION DURING REGENERATION OF QUINHYDRONE ABSORBING SOLUTION IN THE APPARATUS WITH A CONTINUOUS BUBBLING LAYER

Andriy Slyuzar^{1, ⊠}, Zenoviy Znak¹, Yaroslaw Kalymon¹, Andriy Helesh¹

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Abstract. The enhancement factor of air oxygen absorption by quinhydrone absorbing solution in the apparatus with a continuous bubbling layer and the rate constant for the reaction of chemisorbed oxygen and the reducing form of quinhydrone oligomers have been determined. The obtained results are of practical importance for the choice of mass-transfer apparatus for the regeneration of quinhydrone absorbing solution when removing hydrogen sulfide from gases.

Keywords: oxygen chemisorption, absorbing solution, regeneration, quinhydrone, oligomers, bubbling layer.

1. Introduction

As a result of natural chemical and biological processes during the industrial processing of mineral and organic raw materials, sulfurous compounds contained in raw materials are more often converted into hydrogen sulfide, which accumulates in gas or liquid phases. Due to the high toxicity of hydrogen sulfide, its removal from gases is vitally needed. Moreover, the removed hydrogen sulfide may be used for the production of sulfur or sulfuric acid [1, 2].

Liquid-phase oxidative methods (Lo-Cat, Stretford, Takahaks, Thylox, Unisulf, *etc.*) are of significant practical interest for the purification of oxygen-free sulfurcontaining gases (natural, petroleum, coke, *etc.*) [3-7]. The quinhydrone method of hydrogen sulfide removal, developed at Lviv Polytechnic National University, can compete with the best world analogs [1, 2, 8].

This method is based on the chemisorption of hydrogen sulfide from gas by soda solution of quinhydrone $(1^{st} stage)$:

 $H_2S + Na_2CO_3 \Leftrightarrow NaHS + NaHCO_3$ (1)

At the 2nd stage of the process, the chemisorbed hydrogen sulfide is oxidized to sulfur by quinhydrone, and

 \bowtie savasl2000@yahoo.com

at the 3^{rd} stage quinhydrone is regenerated by air oxygen. Actually, not quinhydrone but products of its oligomerization existed in both the oxidation (quinone) and reducing (hydroquinone) forms, participate in the process. The molecular weight of these oligomers varies from 300 to 800 (average value is 400) [2], whereas for quinhydrone it is 218 g/mol. Therefore, the 2^{nd} and 3^{rd} stages can be described by the following equations:



where *n* is the number of oligomer fragments, n = 1-4.

Flow chart of hydrogen sulfide removal from oxygen-free gases by quinhydrone method should include two main apparatuses: absorber and regenerator. Eq. (1) and partially Eq. (2) proceed in the absorber; Eqs. (2) and (3) – in the regenerator. The calculations carried out according to Eqs. (1) and (2) show that in the absorbing solution containing 10–20 kg/m³ of Na₂CO₃ and 5 kg/m³ of quinhydrone the equivalent concentration of chemisorbed hydrogen sulfide is 7–14 times higher than the equivalent concentration of quinhydrone oligomers. It means that the degree of oxidation of chemisorbed hydrogen sulfide in the absorber does not exceed 7.5–15 % and the solution containing a reducing form of quinhydrone oligomers and the main part (85–92.5 %) of chemisorbed hydrogen sulfide is directed to the regenerator.

Two main processes take place in the regenerator: the absorption of air oxygen by quinhydrone absorbing solution and the oxidation of the oligomers reducing form with absorbed oxygen, *i.e.*, the oxygen chemisorption occurs. The most rational mass-transfer apparatus for the chemisorption process is an apparatus where the rates of

¹Lviv Polytechnic National University,

^{12,} S. Bandera St., 79013 Lviv, Ukraine

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abovementioned processes are commensurable [7, 9, 10]. For the removal of hydrogen sulfide by quinhydrone method a proven horizontal absorber with bucket-like dispersers was used [11]. However, in most industrial liquid-phase oxidative processes for the regeneration of absorbing solutions, absorbers with a continuous bubbling layer are usually used [3]. The effectiveness of this type of apparatus for the quinhydrone method is unknown. Therefore, there is a need for conducting studies of oxygen chemisorption by a quinhydrone absorbing solution in this type of mass-transfer apparatus.

The purpose of the research was to determine the enhancement factor of oxygen absorption by quinhydrone absorbing solution in the apparatus with a continuous bubbling layer, as well as the rate constant for the reaction of dissolved oxygen and quinhydrone oligomers. It was also necessary to study the rate of oxygen absorption by the absorbing solution without quinhydrone oligomers (soda solution) and the rate of oxygen chemisorption by quinhydrone solution saturated with hydrogen sulfide at different air flow rates.

2. Experimental

2.1. Materials

Soda solution ($10 \text{ kg/m}^3 \text{ Na}_2\text{CO}_3$) was obtained by dissolving soda in distilled water. Before the experiments it was boiled for degassing from dissolved oxygen, and then cooled in the absence of air to a given temperature.

Quinhydrone solution was obtained from a solution of oligomerized quinhydrone [2, 8]. For this purpose, quinhydrone - the molecular complex of quinone and hydroquinone $C_6H_4O_2 \cdot C_6H_6O_2$ was dissolved in the soda solution, providing the ratio of soda: quinhydrone = 2:1 (mol/dm^3) . This solution was kept for 7 days with air access under periodic stirring. The oxidation-reducing properties of the resulting solution of quinhydrone oligomers were controlled by the cyclic voltammetry method [8]. The resulting product was used to obtain a quinhydrone solution with concentrations of 10 kg/m^3 of Na_2CO_3 and 5 kg/m^3 of quinhydrone. Before the experiments the quinhydrone solution was saturated with hydrogen sulfide. For this purpose, a mixture of natural gas and hydrogen sulfide was bubbling through a solution to achieve the hydrogen sulfide concentration of 0.85 kg/m³. Hydrogen sulfide was obtained by decomposition of sodium sulfide solution with 20% solution of sulfuric acid.

All reagents were of chemically pure grade.

2.2. Methods

The experiments were carried out at the laboratory setup, the main apparatus of which was a hollow glass

column with an internal diameter of 0.035 m and height of 0.5 m. At the bottom of the column a bubbler was mounted, through which the air or the mixture of natural gas with hydrogen sulfide were supplied. The bubbler was made in the form of a porous glass plate with the thickness of ~5 mm and pore size of 0.2–0.6 mm.

In the first series of experiments the effect of air flow rate (solution gas content) on the rate of oxygen absorption by soda solution was studied. The experiments were carried out at the following constant parameters: temperature 290 K, solution height in a column 0.25 m, solution volume $2.4 \cdot 10^{-4}$ m³, absorption time 480 s. The air flow rate was $(0.78-1.83) \cdot 10^{-6}$ nm³/s, which was controlled by the rheometer. The dissolved oxygen content was determined before and after the experiments using Winkler method and the EZODO 7031 oxygen meter.

In the second series of experiments the effect of air flow on the rate of oxygen chemisorption by quinhydrone absorbing solution was studied. The research parameters were the same as those in the first series, which made it possible to provide the same contact surface of phases and compare the processes. The oxygen chemisorption time was increased to 1800 s. The dissolved hydrogen sulfide content was determined before and after the experiments. For this purpose, the sample solution was placed in a flask, acidified with HCl solution to pH = 2.5-3, and nitrogen was bubbled through it. The content of hydrogen sulfide in the recovered nitrogen-hydrogen sulfide mixture was determined by iodometric method using a solution of cadmium acetate as a hydrogen sulfide absorber, and then converted to its concentration in solution.

2.3. Calculation Methods and Processing of Experimental Results

The description of oxygen chemisorption process by quinhydrone absorbing solution saturated with hydrogen sulfide requires the solution of the equations of dissolved oxygen and quinhydrone oligomers diffusion transfer, as well as the chemical kinetics of the reaction (3). For the analytical solution of such equations the simplified models are used, which are based on assumptions regarding the medium movement, the geometric form of the interphase surface, *etc.* To describe the oxygen chemisorption by the absorbing solution, we chose a two-film model, which is more illustrative and based on a simpler mathematical model [9].

To calculate the absorption enhancement factor χ the values of liquid-side mass-transfer coefficients in the chemisorption (β_L^{chem}) and absorption (β_L^{abs}) processes are used. Both liquid-side and gas-side mass-transfer coefficients are related to the gas sorption rate according to the basic mass-transfer equation [9]:

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$$\frac{dN_{O_2}}{d\tau} = \frac{1}{\frac{1}{\beta_G'} + \frac{m_{pC}}{\beta_L}} \cdot F \cdot \Delta P \tag{4}$$

where N_{O2} is the amount of absorbed oxygen, mol; τ is time, s; β_G' is a gas-side mass-transfer coefficient, mol/(m²·s·Pa); β_L is a liquid-side mass-transfer coefficient, m/s; m_{pC} is the constant of the phase equilibrium, m³·Pa/mol; $1/\beta_G'$ and m_{pC}/β_L are gas-side and liquid side mass-transfer resistance, respectively, m²·s·Pa/mol; ΔP is a driving force of the process, Pa; *F* is the surface of mass-transfer, m².

In order to estimate the ratio of gas-side and liquid side mass-transfer resistances (Eq. (4)), we theoretically calculated corresponding mass-transfer coefficients. In order to calculate the gas-side mass-transfer coefficient during the absorption from a single bubble, the following equations are proposed [9]:

$$Sh_{G} = \frac{\beta_{G} \cdot d_{b}}{D_{G}} = \frac{1}{6Fo_{G}} \left[1 - \frac{6}{\pi^{2}} \exp\left(-4\pi^{2} \cdot Fo_{G}'\right) \right]$$
(5)

$$D_G = D_{273} \cdot \left(\frac{T}{273}\right)^{1.75}$$
(6)

$$Fo_G' = \frac{D_G \cdot \tau}{d_b^2} = \frac{D_G}{w_b \cdot d_b}$$
(7)

$$\tau = \frac{d_b}{w_b} \tag{8}$$

$$w_b = 1.5 \left(\frac{\sigma \cdot g \cdot \Delta \rho}{\rho_L^2}\right)^{0.25} \tag{9}$$

where Sh_G is the Sherwood number for the gas phase; Fo_G' is the Fourier number for the gas phase; d_b is a bubble diameter, m; D_G is the coefficient of oxygen molecular diffusion in the air at the experimental temperature, m²/s; D_{273} is the coefficient of oxygen molecular diffusion in the air (273 K and 0.1 MPa) equal to 0.178 · 10⁻⁴ m²/s [9]; τ is a contact time, s; w_b is the bubble floating-up rate, m/s; σ is a surface tension of water at the boundary with air, N/m; g is an enhancement of gravity, m²/s; $\Delta \rho = \rho_L - \rho_G$; ρ_L and ρ_G are water and air density, respectively, kg/m³.

To calculate the liquid-side mass-transfer coefficient (β_L , m/s), the following equations are proposed:

$$Sh_L = \frac{\beta_L \cdot d_b}{D_L} = \frac{1.13}{\sqrt{Fo_L'}} \tag{10}$$

$$D_L = \frac{14 \cdot 10^{-9}}{V_{O_2}^{0.6} \cdot \mu_{H_2O}^{1.1}}$$
(11)

where Sh_G is the Sherwood number for the liquid phase; Fo_G' is the Fourier number for the liquid phase (calculated analogously to Eq. (7) for the gas phase); D_L is the coefficient of oxygen molecular diffusion in water, m²/s; V_{O2} is a molar volume of oxygen in a liquid state at a normal boiling point, $V_{O2} = 25.6 \text{ cm}^3/\text{mol}$; $\mu_{H_2O}^{1.1}$ is a dynamic viscosity of water, mPa·s.

The solution gas content (V, parts of unity) was calculated according to Eq. (12):

$$V = \frac{n \cdot \pi \cdot d_b^3}{6V_L} \tag{12}$$

where *n* is a number of air bubbles in the solution; V_L is a solution volume, m³.

The obtained values were recalculated according to Eqs. (13) and (14) [9]:

$$\beta_G' = \frac{\beta_G}{RT} \tag{13}$$

$$m_{pC} = m_{px} \frac{M_L}{\rho_L} \tag{14}$$

where *R* is the absolute gas constant, R = 8.31 J/(mol·K); *T* is temperature, K; m_{px} is the phase equilibrium constant, $m_{px} = 37900 \cdot 10^2 \text{ kPa } [9]$; M_L is solution molar mass, kg/kmol; ρ_L is solution density, kg/m³.

According to the results shown in [12], as well as our theoretical calculations (see below) by Eqs. (5)-(14), the liquid phase creates a main resistance to the oxygen absorption. In this case, the rate of oxygen mass transfer from the gas to liquid phase is determined by the liquid-side mass-transfer coefficient; the gas phase resistance $1/\beta_G'$ in Eq. (4) can be neglected.

$$\frac{dN_{O_2}}{d\tau} = \frac{\beta_L}{m_{pC}} \cdot F \cdot \Delta P \tag{15}$$

The driving force of oxygen absorption by soda solution at the inlet of the column (ΔP_{in}^{abs}) was calculated as the difference between the partial pressure of oxygen in the air and the average equilibrium oxygen pressure over the solution during the experiment. The driving force of oxygen absorption at the outlet of the column (ΔP_{out}^{abs}) was calculated as the difference between the partial pressure of oxygen in the air after the column and the average equilibrium partial pressure of oxygen over the solution during the experiment. The average equilibrium partial pressure of oxygen in the air above the solution was taken as that for water. The partial pressure of oxygen in the air at the outlet of the column was calculated as the difference between the partial pressure of oxygen in the air and the partial pressure, which was reduced due to the oxygen absorption.

Oxygen is absent in the quinhydrone solution containing hydrogen sulfide (within the studied concentrations). Therefore, the driving force of oxygen chemisorption by a quinhydrone solution at the column inlet (ΔP_{in}^{chem}) is equal to the partial pressure of oxygen in the air, and the driving force at the column outlet (ΔP_{out}^{chem}) is the difference between the partial pressure of oxygen in the air and the partial pressure, which was

reduced due to the oxygen chemisorption. The average driving force of absorption (ΔP^{abs}) or chemisorption (ΔP^{chem}) was defined as the arithmetic mean of the driving forces at the inlet and outlet, since these values differ by no more than 1.2 times.

The amount of chemisorbed oxygen was calculated from the number of oxidized chemisorbed hydrogen sulfide.

We investigated the absorption and chemisorption of oxygen by sodium and quinhydrone solutions respectively, under bubble-jet mode, which made it impossible to accurately determine the size and number of the bubbles and, hence, the contact surface of the phases. Therefore, the experiments were carried out with the same contact surface of the phases both for absorption and chemisorption processes (the same apparatus, air flow rate, temperature, volume of solutions, soda concentration, *etc.*). According to the experimental results the product of the liquid-side masstransfer coefficients and the contact surface of the phases (F_i) was determined. The ratio of products shows the value of absorption enhancement factor χ [9]:

$$\chi = \frac{\beta_L^{chem} \cdot F_i}{\beta_L^{abs} \cdot F_i} = \frac{\beta_L^{chem}}{\beta_L^{abs}} \tag{16}$$

The absorption enhancement factor depends on the parameters R and M [9]. In terms of the two-film model, these parameters for our system have the following physical meaning: R is the ratio of the reaction rate in the film to the rate of oxygen diffusion through the liquid film; M is the ratio of the diffusion rates through the liquid film of the recovered form of quinhydrone oligomers and oxygen.

In the apparatus with a continuous bubbling layer the reaction rate of dissolved oxygen and reducing form of quinhydrone oligomers is significantly higher than the rate of oxygen absorption. For chemisorption processes, where $\chi \ge 5$, the reaction occurs in the liquid film, *i.e.* the concentration of the absorbed substance is equal to zero. According to [9], for the rapid reaction occurring in the film, the enhancement factor χ and the parameters *R* and *M* are related by Eqs. (17)-(19).

$$\chi = \frac{2(M+1)}{1 + \sqrt{1 + 4\left(\frac{M}{R}\right)^2}}$$
(17)

$$M = \frac{C_2}{g \cdot C_1^*} \cdot \frac{D_2}{D_1} \tag{18}$$

$$R = \frac{1}{\beta_L} \sqrt{\frac{2}{m+1} \cdot D_1 \cdot k_1 \cdot C_1^{*m-1} \cdot C_2}$$
(19)

where C_1^* is the concentration of oxygen at the interface between the gas and liquid phases (it is taken equal to the concentration of saturation), mol/m³; C_2 is the concentration of oligomers reducing form in the solution flow core, mol/m³; *g* is the number of hydroquinone groups of oligomer reacted with oxygen according to Eq. (3); D_1 and D_2 are the diffusion coefficients of oxygen and the reducing form of quinhydrone oligomers in a solution, respectively, m²/s; k_1 is the reaction rate constant; *m* and *n* are the reaction order with respect to the corresponding concentrations.

Eq. (19) allows to calculate the rate constant k_1 for the reaction of dissolved oxygen and the reducing form of the quinhydrone oligomers.

3. Results and Discussion

The results calculated according to Eqs. (5)-(14) are given in Table 1. As it was expected, during air oxygen absorption by soda solution in the apparatus with a continuous bubbling layer, at low gas content the liquid-side mass-transfer resistance is by $(1.9-2.7)\cdot10^3$ times greater than the resistance of the gas phase. With a decrease in the bubbles diameter the gas-side and liquid-side mass-transfer coefficients are increased. However, the increase in β_L value is sharper. Thus, with the decrease in the bubbles diameter from 0.006 to 0.002 m the value of β_G increases by 1.37 times, and β_L – by 1.73 times.

The experimental results and calculations according to Eq. (15) are presented in Table 2. One can see that with increasing air flow rate the product of the liquid-side mass-transfer coefficient and the bubbles surface slightly increase. For example, with the 2 time increase in air flow rate (from $0.78 \cdot 10^{-6}$ to $1.56 \cdot 10^{-6}$ m³/s), the product $\beta_L^{abs.}F_i$ increases from $2.285 \cdot 10^{-7}$ to $2.815 \cdot 10^{-7}$ (m/s)·m², *i.e.*, only by 1.23 times. This is obviously due to the fact that the increase in air flow rate (gas content) increases the masstransfer surface, and simultaneously contributes to the coalescence of the bubbles, which reduces the actual mass-transfer surface.

An important index of the absorption process is the absorption degree and the amount of absorbed oxygen (Table 2). The degree of oxygen absorption is low (less than 0.8 %) and increases with the decrease in air flow rate (gas content). Thus, for air flow rates of $0.78 \cdot 10^{-6}$ and $1.56 \cdot 10^{-6}$ m³/s, the absorption degree is 0.790 and 0.471 %, respectively. The low degree of oxygen absorption is evidently due to the high liquid-side mass-transfer resistance and small height of the bubbling (0.25 m), and, as it was mentioned above, the bubbles coalescence takes place with the increase in gas content. The amount of absorbed oxygen increases slightly with increasing air flow rate.

Table 1

Bubbles diameter	Number of bubbles <i>n</i>	Gas content V, parts of	Gas-side mass-transfer coefficients		Liquid-side mass-transfer coefficient	Gas-side mass- transfer resistance	Liquid-side mass- transfer $(m_r c/\beta_I) \cdot 10^{-8}$.	
$d_b \cdot 10^3$, m		unity	$\beta_G \cdot 10^2,$ m/s	$\beta'_{G} \cdot 10^{\circ},$ mol/(m ² ·s·Pa)	$\beta_L \cdot 10^4$, m/s	$(1/\beta_G) \cdot 10^{-5}$, m ² ·s·Pa/mol	m ² ·s·Pa/mol	
2	5	$1.75 \cdot 10^{-5}$		1.488	5.365	0.672	1.269	
	15	5.23·10 ⁻⁵	3.586					
	50	$1.75 \cdot 10^{-4}$						
4	5	$1.39 \cdot 10^{-4}$	2.966	1.231	3.794	0.812	1.795	
	15	$4.19 \cdot 10^{-4}$						
	50	1.39.10-3						
6	5	$4.71 \cdot 10^{-4}$		1.089	3.097	0.918	2.199	
	15	$1.41 \cdot 10^{-3}$	2.624					
	50	$4.71 \cdot 10^{-3}$						
10	5	$2.18 \cdot 10^{-3}$	2.278	0.945	2.399	1.058	2.838	
	15	$0.65 \cdot 10^{-2}$						
	50	$2.18 \cdot 10^{-2}$						

The results calculated according to the criterial equations of mass transfer*

*Calculations are made for such constant parameters: temperature 290 K; solution concentration 10 kg/m³ Na₂CO₃.

The experimental results and calculations of air oxygen chemisorption by quinhydrone absorbing solution show (Table 3) that the product of the liquid-side masstransfer coefficient and the bubbles surface increases slightly with increasing air flow rate, the same as for the absorption process. For example, with the increase in air flow rate by more than 2 times (from $0.78 \cdot 10^{-6}$ to 1.83.10⁻⁶ m³/s), the product $\beta_L^{chem} F_i$ increases by only 1.19 times. The rest of the chemisorption parameters (the amount of chemisorbed oxygen per unit time, the chemisorption degree, the driving force of the process, the amount of chemisorbed oxygen) are changing similar to the corresponding parameters of absorption. However, there is a big difference between the absolute values of these processes. Thus, at the same air flow rate (the same gas content, the size and surface of the bubbles), the degree of oxygen chemisorption is higher by 5.7-6.6 times in comparison with the absorption process. The values of chemisorbed oxygen amount per time unit and chemisorption driving force are also higher. The liquidside mass-transfer coefficient is $\beta_L^{chem} = 1.04 \cdot 10^{-4}$ m/s.

The main result of oxygen absorption (Table 2) and chemisorption (Table 3) studies in the apparatus with a continuous bubbling layer is the determination of the absorption enhancement factor, the average value of which is 5.14.

Calculations of the parameters M and R by Eqs. (18) and (17), respectively, show that M = 9.95 and R = 6.42. For calculations by Eq. (18) the following values were taken: $D_1 = 1.8 \cdot 10^{-9} \text{ m}^2/\text{s}$; $C_2 = 12.5 \text{ mol/m}^3$; $C_1^* = 0.307 \text{ mol/m}^3$; g = 2. In literature sources there are no data regarding the diffusion coefficients of quinhydrone oligomers in water, so we used the diffusion coefficient of sucrose $C_{12}H_{21}O_4$ – a substance which is close to them with respect to solubility and molecular weight, $D_2 = 0.88 \cdot 10^{-9} \text{ m}^2/\text{s}$ [9]. The obtained values of $M > R > \chi$ indicate that the reaction between the dissolved oxygen and the reducing form of oligomers has a high rate and ends in the liquid film. The partial oxygen pressure over the quinhydrone solution containing chemisorbed hydrogen sulfide is equal to zero [9].

To calculate the rate constant using Eq. (19), we adopt m = 1 and n = 1, which is characteristic of similar chemisorption processes [9]. By comparing the values of oxygen concentration C_1^* and quinhydrone oligomers concentration C_2 , it can be assumed that C_2 is constant and the chemical reaction proceeds by the pseudo first order with the rate constant $k_2 = k_1 \cdot C_2$. Then Eq. (19) can be written as follows:

$$R = \frac{1}{\beta_L} \sqrt{D_1 \cdot k_2} \tag{20}$$

The results of calculations are given in Table 4.

The increase in air flow rate results in the increase of oxygen chemisorption rate. For example, the increase in the air flow rate by 2 times (from $0.78 \cdot 10^{-6}$ to $1.56 \cdot 10^{-6}$ m³/s) leads to 1.33 time increase in the chemisorption rate (from $1.39 \cdot 10^{-3}$ to $1.85 \cdot 10^{-3}$ mol/(m³·s).

The reaction rate of chemisorbed oxygen and reducing form of quinhydrone oligomers is much greater than the oxygen chemisorption rate. With increasing air flow rate the ratio of chemical reaction rate to the oxygen chemisorption rate decreases. For the same size of bubbles this ratio does not depend on the air flow rate. This fact again confirms the coalescence of the bubbles with increasing air flow rate. Under bubbling mode of chemisorption, which is observed at air flow rate below $0.78 \cdot 10^{-6} \text{ nm}^{-3}/\text{s}$, and the bubbles size of 0.002 m the ratio $v_r/v_{chem} \ge 427$. This ratio unambiguously indicates that the resistance to oxygen chemisorption is concentrated in a liquid film.

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Product of the liquid-side mass transfer coefficient and the bubbles surface $(\beta_L^{abx} F_i) 10^7$, (m/s) m ²			2.484	2.571	2.815	2.821
Amount of	5.779	6.171	6.354	6.890	6.950	
Average	17224	16920	16830	16668	16775	
	0.790	0.627	0.484	0.471	0.405	
Amount of absorbed oxygen $\Delta N 10^5$, mol			2.962	3.050	3.307	3.336
Oxygen concentration in solution C_l , mol/m ³	after absorption	0.1312	0.1406	0.1447	0.1550	0.1550
	before absorption	0.0156	0.0172	0.0176	0.0172	0.0160
Amount of oxygen supplied to the column N'10 ³ , mol			4.725	6.300	7.020	8.235
Bubbles	F_1	F_2	F_3	F_4	F_5	
Gas content	3.12	4.46	5.95	6.63	7.73	
Air flow	rate $V_{air} 10^6$, nm ³ /s	0.78	1.05	1.40	1.56	1.83
	Air Gas Amount of Ruhhles Oxygen concentration in solution C ₁ , mol/m ³ Amount of absorbed Average Aniving Average	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Air fow fow $V10^3$, surface $W10^3$, E_i , m2Amount of solution to F_i , m2Amount of solution to beforeAmount of absorbed absorbedAverage driving desree, % absorptionAnount of driving desree, % absorptionProduct of the liquid-side mass- transfer coefficient and the transfer coefficient and the force of absorptionNo V_{ui} : $U_{air}^{air}:10^6$, of m1/sBubbles V_{10}^{air} , m2Amount of absorptionProduct of the liquid-side mass- driving desree, % absorptionNo $V_{air}:10^6$, of m1/s V_{10}^3 , molt M_{10}^3 , molt M_{10}^3 , molt M_{10}^3 , molt M_{10}^3 , molt M_{10}^3 , moltNo 0.78 3.12 F_1 3.510 0.1312 2.774 0.790 17224 5.779 2.285	Air flow tion $V10^3$, $V10^3$, E_i , m2Amount of solution to F_i , m2Amount of solution to $V10^3$, $V_{atr}^{-1}10^6$, $V_{atr}^{-1}10^6$, partsAmount of trunc F_i , m2Amount of solution C_i, mol/m3Product of the liquid-side mass- driving degree, % degree, %Average driving degree, % degree, %Amount of trunce of absorbionProduct of the liquid-side mass- transfer coefficient and the per time unit mol $V_{atr}^{-1}10^6$, $V_{atr}^{-1}10^6$, of m3/s R_i , m2 $V_{atr}^{-1}10^3$, mol $Mount ofbeforeProduct of the liquid-side mass-degree, %AN/10^5,AD/10^5,AD/10^5,AverageabsorptionAmount oftransfer coefficient and thetransfer coefficient and theAN/10^5,AD/10^5,AD/10^5,0.783.12F_13.5100.01560.13122.7740.790172245.7792.2850.784.46F_24.7250.01720.14062.9620.627169206.1712.484$	Air flow $V10^3$ Gas content $V10^3$ Amount of solution CAmount of solution CAmount of absorbedProduct of the liquid-side mass- driving absorbedflow $V10^3$ $V10^3$ Bubbles oxygen parts x^{Merage} F_{I}, m^2 Amount of solution CProduct of the liquid-side mass- diving absorbed $V_{air}'10^6$ nin^3/s $Bubbles$ parts E_{I}, m^2 F_{I}, m^2 Amount of solutionProduct of the liquid-side mass- degree, % absorptionAverage diving absorptionAmount of absorptionProduct of the liquid-side mass- transfer coefficient and the per time unit D^{air}, Pa $V_{air}'10^6$ $ninityF_{I}, m^2F_{I}, m^2BubblesabsorptionAmount ofabsorptionProduct of the liquid-side mass-degree, %D^{air}, PaAverageabsorption,D^{air}, PaAverageabsorption,D^{air}, PaAverageabsorption,D^{air}, PaV_{air}'10^6ninityF_{I}3.12F_{I}3.5100.01560.13122.7740.790172245.7792.2851.05F_{3}6.3000.01760.14473.0500.484168306.3542.571$	Air flow $V10^3$ Gas content surface $rindAmount ofsolution C, mol/m³Amount ofabsorbedabsorbedAveragedrivingabsorbeddrivingAmount ofdrivingabsorbedforce ofbeforeProduct of the liquid-side mass-drivingabsorbedabsorbionIowV10^3V10^3surfaceVin^3/sBubblessolution C, mol/m³absorbionAmount ofabsorbionabsorbionAverageabsorbionabsorbionAmount ofabsorbionabsorbionProduct of the liquid-side mass-drivingabsorbionV_{air}:10^6nin^3/sunityF_1, m²N10^3, molAmount ofsolutionProduct of the liquid-side mass-degree, %absorption,\Delta N/r10^8, mol/sProduct of the liquid-side mass-transfer coefficient and theper time unit\Delta N/r10^8, mol/sV_{air}:10^6nin^3/snin^3/sF_13.5100.01560.13122.7740.790172245.7792.2850.781.56F_24.7250.01720.14062.9620.627169206.1712.4841.6668F_47.0200.01720.15503.3070.471166686.8902.815$

Effect of air flow rate on the oxygen chemisorption by quinhydrone solution	Average value of acceleration factor χ_{aver}	5.14			
	Acceleration factor χ	4.85	4.95	5.37	5.21
	Product of the liquid-side mass-transfer coefficient and the bubbles surface $(\beta_L^{chem}, F_i) 10^7, (m/s) \text{m}^2)$	11.10	12.29	13.80	14.66
	Amount of chemisorbed oxygen per time unit $\Delta N/\tau 10^7$, mol/s	3.339	3.711	4.167	4.444
	Average driving force of chemicroption, ΔP^{chem} , Pa	20520	20600	20666	20675
	Chemisorption degree, %	4.57	3.79	3.18	3.09
	Amount of chemisorbed oxygen ΔN10 ⁴ , mol	6.01	6.68	7.50	8.00
	sulfide oxidized hydrogen sulfur $G 10^5$, kg	4.09	4.54	5.10	5.44
	Amount of oxygen supplied to the column $N \cdot 10^2$, mol	1.3162	1.7720	2.3615	2.6325
	Bubbles surface F_i , m ²	F_1	F_2	F_3	F_4
	Gas content $V10^3$, parts of unity	3.12	4.46	5.95	6.63
	Air flow rate, $V_{air}^{air} 10^6$, nm ³ /s	0.78	1.05	1.40	1.56

5.33

15.05

4.572

20720

2.67

8.23

5.60

3.0881

 F_5

7.73

1.83

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Table 3

Table 2

Table 4

Air flow rate V_{air} 10 ⁶ , nm ³ /s	Oxygen chemisorption rate	Reaction rate constants		Ponction rate	Patio	
	$v_{chem} \cdot 10^3$, $v_{chem} = \Delta N / (\tau V_s)$, mol/(m ³ ·s)	$k_1, \mathrm{m}^3/(\mathrm{s}\cdot\mathrm{mol})$	k_2, s^{-1}	$v_r = k_1 \cdot C_1^* \cdot C_2, \text{ mol/(m}^3 \cdot s)$	U_r/U_{chem}	
0.78	1.390				427	
1.05	1.546				384	
1.40	1.736	0.1547	17.41	0.593	342	
1.56	1.852				320	
1.83	1.905				311	

The calculated kinetic values for the reaction of dissolved oxygen and reducing form of quinhydrone oligomers

4. Conclusions

The mass transfer coefficients in gas and liquid phases during oxygen absorption with soda solution were calculated. It is shown that the resistance of the liquid phase is by $(1.9-2.7)\cdot 10^3$ times greater than the resistance of the gas phase. The enhancement factor of oxygen absorption during the regeneration of a quinhydrone solution in the apparatus with a continuous bubbling layer was found to be 5.14, indicating that the chemical reaction between absorbed oxygen and the reducing form of quinhydrone oligomers occurs in a liquid film with a high rate. The rate constant for the reaction of chemisorbed oxygen and the reducing form of quinhydrone oligomers was found to be 0.1547 $m^3/(s \cdot mol)$. In the apparatus with a continuous bubbling layer, the liquid-side resistance during oxygen absorption is large, which does not provide the necessary rate of quinhydrone solution regeneration. Therefore, this type of mass-transfer equipment can not be recommended for regeneration of absorbing solution used in quinhydrone method of hydrogen sulfide removal from gases.

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ДОСЛІДЖЕННЯ ХЕМОСОРБЦІЇ КИСНЮ ПІД ЧАС РЕГЕНЕРАЦІЇ ХІНГІДРОННОГО ПОГЛИНАЛЬНОГО РОЗЧИНУ В АПАРАТАХ З СУЦІЛЬНИМ БАРБОТАЖНИМ ШАРОМ

Анотація. Визначено коефіцієнт прискорення абсорбції кисню повітря хінгідронним поглинальним розчином в апараті з суцільним барботажним шаром, а також константу швидкості реакції між хемосорбованим киснем і відновною формою олігомерів хінгідрону. Отримані результати мають практичне значення для вибору масообмінного апарату для регенерації поглинального розчину у хінгідронному методі очищення газів від сірководню.

Ключові слова: хемосорбція кисню, поглинальний розчин, регенерація, хінгідрон, олігомери, барботажний шар.