

**Botagoz M. Kaldybayeva¹, Alisher E. Khussanov¹,
Arlan Zh. Abilmagzhanov², Stanislav Boldyryev³**

¹M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan;

²Institute of Fuel, Catalysis and Electrochemistry. D. Sokolskogo, Kazakhstan;

³Centre for Sustainable Development of Energy, Water and Environment Systems, Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Zagreb, Croatia.

khusanov_1975@inbox.ru, kaldybaeva.b@mail.ru, arlandez_81@mail.ru,
Stanislav.Boldyryev@fsb.hr

EXPERIMENTAL JUSTIFICATION OF THE ABSORBER SELECTION FOR THE PROCESS OF SIMULTANEOUS CHEMISORPTION OF HYDROGEN SULPHIDE AND CARBON DIOXIDE

Abstract. In this article, the objects of research are combined membrane-absorption processes with a chemical reaction and chemisorption plants for the purification of multicomponent gas mixtures. The subject of the research were the processes of removal of H₂S and CO₂ from multicomponent gases.

The results of studying the features of simultaneous absorption of H₂S and CO₂ by an aqueous solution of NaOH are carried out. With the subsequent analysis and selection of the main parameters of the extraction process of H₂S.

With the simultaneous absorption of H₂S and CO₂, it is established that the chemical capacity of the absorption solution decreases with respect to H₂S. The rate and concentration constants for the absorption of H₂S and CO₂

Key words: chemisorption, chemisorb, absorber, multicomponent gas, mass transfer, microburnage process, alkali, liquid, gas.

Introduction

Existing processes of the removal of H₂S from multicomponent gases for a variety of process, technic-economic indicators cannot be recommended for the purification of a relatively small amount of gas in the composition of the gases being cleaned. The task of removing H₂S from the composition of multicomponent gases is often complicated due to the CO₂ in the composition. In this case, one of the most appropriate methods is removing H₂S with a chemical absorber due to the reaction in the liquid phase.

For the absorption of H₂S in industry traditionally aqueous solutions of carbonates (Na₂CO₃, K₂CO₃), ethanol amines, ammonia, oxysulfo-arsenic sodium (or ammonium), etc. are used [1-3]. The carbonate method is used to purify gases containing carbon dioxide, which is necessary to ensure the reversibility of the process during the regeneration of the absorbent. This process has a limitation on the partial pressure of CO₂ in the source gas, which determines the residual content of H₂S in the purified gas [4].

Methods

The most active absorber of the acidic components of gases is an aqueous solution of alkali. NaOH in an aqueous solution irreversibly interacts with hydrogen sulfide by known reactions:



The presence of CO₂ in the gas composition, it is absorbed by the alkaline solution by the reactions:



Absorption of H₂S and CO₂ from gas with NaOH solution is related to chemisorption. The study of absorption, followed by a chemical reaction in the liquid phase, has been the goal of numerous studies. The most important of them are the works of Chisinau [5, 6] and Dankverts [7, 8]. In this paper, an attempt was made to combine the description of the processes of adsorption and absorption from a single point of view [9]. The difficulty of studying the processes of gas absorption by solutions of absorbents is related to the fact of a chemical reaction in the absorption process has a significant effect on both the equilibrium between the phases and the kinetics of absorption. In this case, the absorption rate is determined not only by the rate of mass transfer, but also by the kinetic laws of the reaction. This study aimed studying the joint absorption of H₂S and CO₂ by aqueous-alkaline solutions are relevant.

When a reaction occurs between the dissolved gaseous component and the absorber in the liquid phase, part of the component goes into a bound state and the concentration of the free component in the liquid decreases. Such decrease leads to an increase of the concentration gradient and an acceleration of the absorption in the phase. This acceleration is greater, the higher the rate of chemical reaction [6]. The mass transfer equation for the absorption of H₂S and CO₂ by the solution of NaOH can be written as:

$$W_A = K_p F [p - m_{pe}(C - \delta)], \quad (5)$$

where W_A – the amount of the absorbed substance, kmol/s; K_p – the mass transfer coefficient; F – phase contact surface, m²; p – partial pressure, Pa; C – concentration of unbound component, kmol/m³; δ – coefficient for increasing the driving force in the liquid phase of equilibrium, m³Pa/kmol.

Results

The chemisorption analysis is carried out by considering the diffusion equations for the absorbed component A (H₂S and CO₂) and the active part of the absorber B (NaOH) together with the kinetic equation of reaction (6):

$$\frac{L}{G} = \frac{n_{\text{H}_2\text{S}}(C_{\text{H}_2\text{S}_0} - C_{\text{H}_2\text{S}_1}) + n_{\text{CO}_2}(C_{\text{CO}_2_0} - C_{\text{CO}_2_2})}{C_{\text{OH}_1} - C_{\text{OH}_0}} \quad (6)$$

The study of the kinetics of the absorption of CO₂ and H₂S with a NaOH solution was considered in detail in [10–15]. However, the results of individual studies differ widely among themselves and many of them can only be used to qualitatively characterize the process.

The main objective of this study is an identification of the features of simultaneous absorption of H₂S and CO₂ with NaOH solution, followed by analysis of the data studied and selection of the main parameters of the process for deep extraction of H₂S.

The experiments were carried out on an experimental unit in which model gas mixtures were passed through a chemisorber with measurement of the volume of the leaked gas and simultaneous determination of the composition of the absorption solution in the ceramic sorbent with a ceramic membrane according to MVI "Methodology for measuring the concentrations of sulfide and mercaptide sulfur in alkaline solutions" (Certificate - metrological center No. 1106-02 dated 12.25.01.) and chromatographic analysis of the gas phase [16, 17] at the exit from the unit. The balance of the products of the absorption of H₂S and CO₂, analytically established in the study of the alkaline solution at the end of each experimental cycle, correlated with the amount and composition of the gas passed through the chemisorber. All model mixtures were prepared in an accredited laboratory "Testing Regional Laboratory of Engineering Profile" Constructional and Biochemical Materials "(IRLIP" KBM ") at SKSU them. M. Auezov.

The experiments of the absorption study of aqueous alkaline solutions of H₂S from the gas phase were carried out with use of model mixtures of different composition. 10% of the mass was used as the absorption solution. An aqueous solution of NaOH, for the preparation of which sodium hydroxide was used according to GOST 4328 of the "analytically clean" and distilled water. The content of NaOH in the

absorption solution was determined by the method of volumetric titration with 1 N hydrochloric acid solution using thymolphthalein and methyl orange.

The main parameters of the unit: absorption mode – bubbling; gas flow rate of 90-120 l/h; temperature 25 °C; pressure 0.1 MPa. A 10% aqueous solution of NaOH was loaded into a chemisorber equipped with a Schott filter to ensure a uniform gas supply. At the outlet of the chemisorber, a Drexel flask was filled with an indicator 10% aqueous solution of cadmium chloride to capture H₂S “leakage”, after which a model gas mixture (N₂ + H₂S + CO₂) was fed from a cylinder through a reducer and a rotameter. The gas flow rate corresponding to the bubbling mode without the entrainment of liquid was set using the fine adjustment valve and controlled according to the readings of the rotameter. The amount of gas passed was determined by a gas flowmeter. Periodic analysis of the absorption solution was carried out on the content of sodium sulphides and caustic soda, and the gas mixture on the content of H₂S and CO₂ after chemisorption.

To control the content of H₂S and CO₂ in the gas after chemisorption, a chromatographic analysis method with a mass spectrometric detector (MSD) was used on a ShimadzuGSMS-2010 chromatograph.

At the initial stage of the study, experiments were carried out on the chemisorption of H₂S from a model mixture of gases of composition No. 1 (% mass.): N₂-97.15; H₂S - 2.85 and gas consumption 120 l/h.

It has been established that the reaction of absorption of H₂S by an alkaline solution proceeds intensively up to the complete consumption of the active alkali. The sharp decrease in the degree of absorption, characterized by a break in the curve and an increase in the concentration of H₂S in the gas at the outlet of the chemisorber, is associated with a decrease in the driving force of the process in the liquid phase. One of the factors affecting the decrease in the chemisorption capacity of the absorption solution can be a change in its viscosity, which, in turn, leads to an additional diffusion resistance to the transfer of the absorbed component to the active component (NaOH) of the absorber [18].

When studying the absorption of H₂S from the gas mixture of composition No. 2 (wt.%): N₂ - 94.05; H₂S - 3.05; CO₂ - 2.9 (Figures 2, 3) it was found that in parallel with reactions (1, 2) slower reactions of (3, 4) NaOH solution with CO₂ take place.

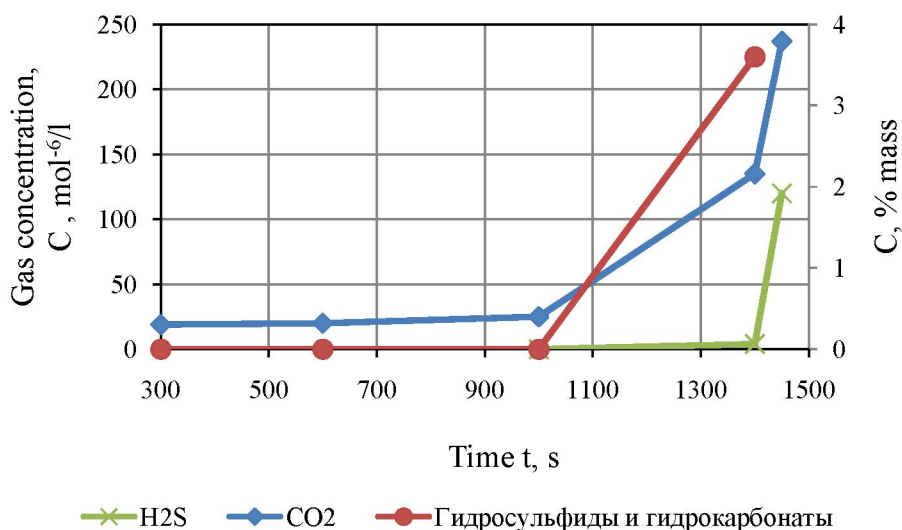


Fig. 1 - Changes in the concentrations of H₂S (1) and CO₂ (2) in the model gas mixture No. 2 and the sum of hydrosulfides and hydrocarbonates (3) in the absorption solution in time

The most important result of the experiments was the establishment of a joint effect of two acid gas impurities on the results of liquid-phase chemisorption absorption, as well as the possibility of absorption of H₂S in the absence of free alkali in solution. With simultaneous absorption of H₂S and CO₂, the chemical capacity of the absorption solution in relation to hydrogen sulfide decreases, which is associated with the occurrence of reactions (3, 4).

Assuming the absorption of H₂S in the initial period occurs by an instantaneous reaction of zero order and then the rate of concentration increase in the purified gas (the reciprocal of the component's chemisorption constant) is calculated by the formula [19]:

$$k_{H_2S} = \frac{1}{t}(C_{H_2S}^0 - C_{H_2S}), \quad (7)$$

and the concentration of H_2S of the purified gas is determined by the following equation [18]:

$$C_{H_2S} = C_{H_2S}^0 - k_{H_2S} \cdot t \quad (8)$$

The calculation of the rate constant and concentration at the absorption of CO_2 is done similarly. Analyzing the change of H_2S and CO_2 concentrations in the purified gas over time (Fig. 1), we can distinguish three characteristic areas, which are reflected in the change of the composition of the absorption solution.

At region I, there is a complete absorption of H_2S , more selective with respect to CO_2 chemisorption, with a decrease in the concentration of active alkali and an increase in sulfide sulfur and sodium carbonate in solution. Hydrosols in the absorption solution in this area were not found. Section II is characterized by a slight decrease in the degree of absorption of hydrogen sulfide, while the CO_2 content increases more significantly, at the same time acid salts — $NaHS$ and $NaHCO_3$ — are found in the absorption solution. It is characteristic that at the end of section II there is no active alkali in the solution, while the absorption of H_2S continues and the “leakage”, that is, a sharp rise in the concentration of H_2S in the purified gas does not occur. This fact is explained by the chemical binding of H_2S with sodium carbonate, formed by reaction (4) in the time interval of the corresponding section I. Based on theoretical assumptions, its interaction with H_2S occurs as follows:



Further, increase in the content of hydrosols in the solution in section III, there is a significant inhibition of the absorption of acidic components, and the concentration of H_2S and CO_2 at the exit of the hemisorber increases sharply at almost the same rate, there is a leakage of H_2S .

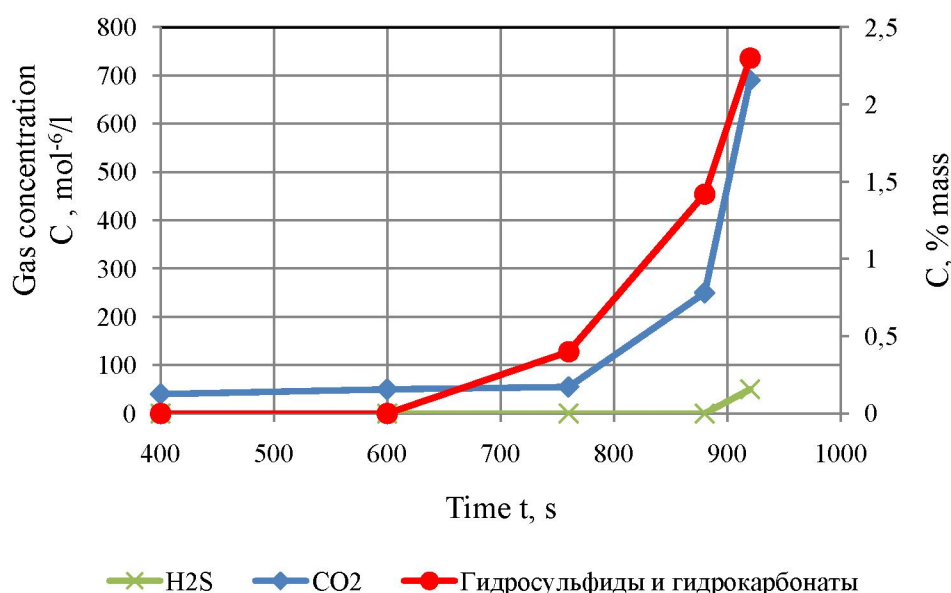


Fig. 2 - Concentration change of H_2S and CO_2 of the model gas mixture No. 3 and the sum of hydrosulfides and hydrocarbonates in the absorption solution with time

At the last stage of the current study (an experiment 3), the kinetics of the absorption of CO_2 and H_2S was studied on a model mixture with a modified ratio of the absorbed components of composition No. 3 (wt. %): N_2 - 91.25; H_2S - 2.8; CO_2 - 5.95. From the data in Fig. 2 it can be seen that with an increase of the CO_2 content from 2.9 to 5.95%, the chemical capacity of a 10% NaOH solution, relative to H_2S , is proportionally reduced. At the same time, all the above designated areas that characterize the change in the

patterns of absorption of H_2S and CO_2 are preserved. As follows from the calculations of k_{H_2S} and k_{CO_2} , which characterize the appearance of acid gases at the outlet of the absorber, the rate of hydrogen sulfide ratio with an aqueous solution of NaOH is substantially higher than the absorption rate.

An increase of the concentration of CO_2 in the source gas does not have a significant effect on the rate of absorption of H_2S , but at the same time the rate of ingestion of CO_2 increases due to an increase in the concentration of CO_2 at the interface. This is determined by the determining factor for the transfer of CO_2 to the active component of the absorber. The chemical capacity of the absorption solution, as in previous experiments, is maintained up to the complete production of the active component NaOH.

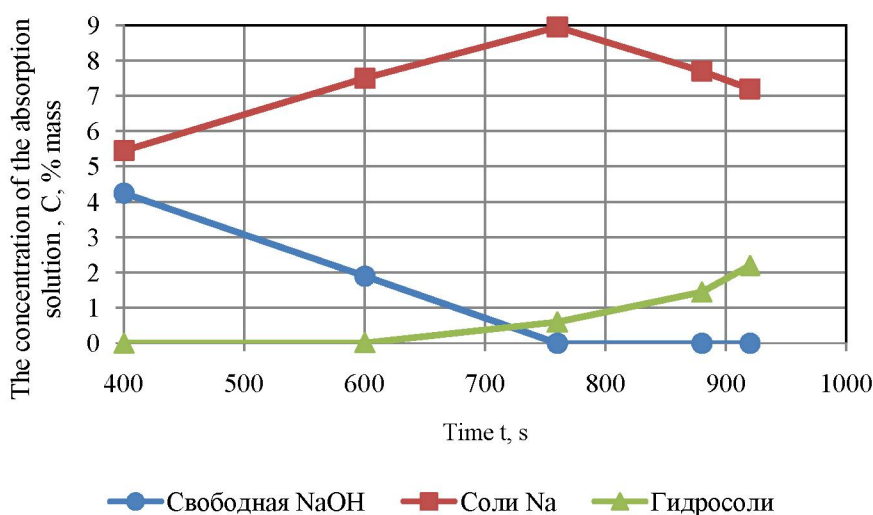


Fig. 3 - Change in the composition of the absorption solution with time (mixture No. 3)

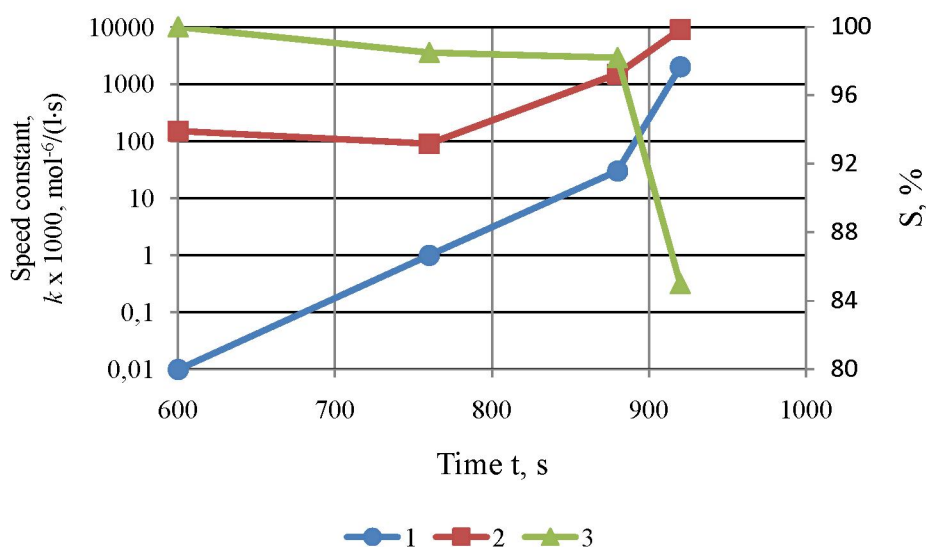


Fig. 4 - The rate constants for the appearance of H_2S and CO_2 at the outlet of the absorption solution (experiment 3); 1 - k_{H_2S} , 2 - k_{CO_2} , 3 - S

When considering the patterns of joint absorption of H_2S and CO_2 with a water-alkaline solution, an attempt was made to interpret the results obtained from the point of view of the selectivity of the chemisorption process.

The physical meaning of the selectivity process of chemisorption S is a ratio of changes in the concentrations of unbound components over time during inhibition of the absorption reactions due to changes in the composition of the water-alkaline phase, which can be described as follows:

$$S = \left(1 - \frac{k_{H_2S}}{k_{CO_2}}\right) \cdot 100\% \quad (10)$$

Selectivity is based on a significant difference in the rate of interaction of CO₂ and H₂S with an alkaline solution.

In Fig. 4 (experiment 3) shown that the selectivity of H₂S decreases by the absorption, but at different rates in the different sections as described earlier.

Table 1- Constants of the velocity concentration of acid gases at the outlet of the absorber and their relationship.

Time, s	Experiment 2			Time, s	Experiment 3		
	k _{H₂S}	k _{CO₂}	k _{H₂S} /k _{CO₂}		k _{H₂S}	k _{CO₂}	k _{H₂S} /k _{CO₂}
	mol ⁻⁶ /(ls)				mol ⁻⁶ /(l s)		
600				400			
1000	3,53·10 ⁻⁶	0,0168	2,1·10 ⁻⁴	600	1,009·10 ⁻⁵	0,111	9,067·10 ⁻⁵
1400	8,41·10 ⁻³	0,277	0,0304	760	1,099·10 ⁻³	0,0815	0,0135
1440	2,873	2,404	1,194	880	0,0283	1,415	0,0198
				920	1,576	10,63	0,148

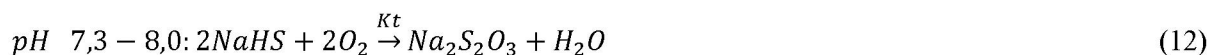
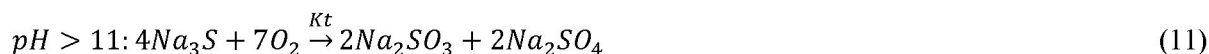
In experiment 3, the concentration of CO₂ in the model mixture is approximately two times higher than the concentration of hydrogen sulfide. At the initial stage of absorption (section I), a decrease in the amount of NaOH and an accumulation of sodium salts occurs (Fig. 2, 3). The concentration gradient and the selectivity of H₂S absorption are maximal. Region II is characterized by the formation of acid salts, their proportion approaches the maximum value (Fig. 3), while the selectivity of chemisorption decreases only slightly, which is associated with the secondary reaction of H₂S with the absorption product of CO₂, which is a sodium carbonate.

Region III reflects a sharp increase of the hydrosulfide and bicarbonate formation due to the consumption of sodium carbonate by the reaction (9). During this period, the selectivity of H₂S absorption decreases sharply, and the concentration of H₂S in the gas to be purified reaches the “slip” value.

Discussion

The experiments showed the complex staged nature of the joint absorption of CO₂ and H₂S from model gas mixtures with a water-alkaline solution and made it possible to determine the boundary conditions of the chemisorption process and selectivity with respect to the key component, which is H₂S.

As a result of the chemical absorption of CO₂ and H₂S by an aqueous-alkaline solution, a solution containing sodium sulfides and carbonates is formed. In order to partially regenerate alkali and neutralize toxic sulfide and sodium hydrosulfide, this solution can be catalytic liquid-phase oxidized with atmospheric oxygen according to the next reactions [15]:



Conclusion

In the result of this study of the kinetics of absorption of CO₂ and H₂S with a 10% aqueous solution of NaOH, it was found that the absorption solution has a high chemical capacity and selectivity for H₂S, which persists until complete binding of the active component NaOH with H₂S, allows you to use this method for the purification of multicomponent gases, which, in addition to H₂S, includes CO₂.

Б.М.Калдыбаева¹, А.Е.Хусанов¹, А.З. Абилямагжанов², С.А.Болдырев³

¹М.Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент қ., Қазақстан;

²Д.Сокольский атындағы отын, катализ және электрохимия институты, Алматы қ., Қазақстан;

³Машина жасау және теңіз архитектурасы факультетінің Энергетика, су және қоршаған орта жүйелерінің орнықты дамуы орталығы, Загребский университеті, Хорватия

КҮКІРТ СУТЕГІ МЕН КӨМІРҚЫШҚЫЛ ГАЗЫН БІРМЕЗГІЛДЕ ХЕМОСОРБЦИЯЛАУ ПРОЦЕСІ ҮШІН СІңІРГІШТІ ТАҢДАУДАҒЫ ТӘЖІРИБЕЛІК НЕГІЗДЕМЕ

Аннотация: Бұл мақалада зерттеу объектілері болып химиялық реакциясымен үлестірілген мембрандық абсорбциялық процестер мен көпкомпонентті газ қоспаларын тазалауға арналған хемосорбциялық жабдықтар табылады. Зерттеу тақырыбы көпкомпонентті газдардан H_2S мен CO_2 айыру процесі болды.

$NaOH$ су ерітіндісімен H_2S және CO_2 бірізгіде сіңіру ерекшеліктерін зерттеудің нәтижелері келтірілді. H_2S бөліп алу процесінің негізгі параметрлерін сараптау мен таңдауға негіздемелер келтірілді. Бір мезгілде H_2S және CO_2 сіңіруімен бірге сіңіру ерітіндісімен химиялық сыйымдылық H_2S қатынасты төмендейді. H_2S және CO_2 сіңірудегі жылдамдық константасы мен концентрация анықталды.

Түйін сөздер: хемосорбция, хемосорбер, сіңіргіш, көпкомпонентті газ, массаалмасу, микробарботаждық процесс, сілтілік, сұйық, газ.

Б.М.Калдыбаева¹, А.Е.Хусанов¹, А.З. Абилямагжанов², С.А.Болдырев³

¹Южно-Казахстанский государственный университет им. М.Ауезова, г.Шымкент, Казахстан;

²Институт топлива, катализа и электрохимии им. Д.Сокольского, Казахстан;

³Центр устойчивого развития систем энергетики, водных ресурсов и окружающей среды, факультет машиностроения и морской архитектуры, Загребский университет, Хорватия

ЭКСПЕРИМЕНТАЛЬНОЕ ОБОСНОВАНИЕ ПОДБОРА ПОГЛОТИТЕЛЯ ДЛЯ ПРОЦЕССА ОДНОВРЕМЕННОЙ ХЕМОСОРБЦИИ СЕРОВОДОРОДА И УГЛЕКИСЛОГО ГАЗА

Аннотация: В этой статье объектами исследования являются совмещенные мембранно-абсорбционные процессы с химической реакцией и хемосорбционные установки для очистки многокомпонентных газовых смесей. Предметом исследований явились процессы удаления из многокомпонентных газов H_2S и CO_2 .

Проведены результаты исследования особенностей одновременного поглощения H_2S и CO_2 водным раствором $NaOH$. С последующим анализом и подбором основных параметров процесса извлечения H_2S .

При одновременной абсорбции H_2S и CO_2 установлено, что химическая емкость поглотительного раствора по отношению к H_2S снижается. Рассчитаны константы скорости и концентрации при поглощении H_2S и CO_2 .

Ключевые слова: хемосорбция, хемосорбер, поглотитель, многокомпонентный газ, массообмен, микробарботажный процесс, щелочь, жидкость, газ.

REFERENCES

- [1] Cole A., Fred S., Riesenfeld L. Gas purification. M.: GNTLiGTL, **1968**. 398 p. (in Russ).
- [2] Kempbell DM Cleaning and processing of natural gases. M.: Nedra, **1977**. 349p. (in Russ).
- [3] Basarygin Yu.M., Budnikov VF, Zakharov AA, Yasyan Yu.P., Zhirnova AP, Karepov AA, Myasitsin Yu.G. // Oil refining and petrochemistry. **2004**. №12. P.48-49. (in Russ).
- [4] Technology of processing natural gas and gas condensate: a reference book in 2 hours. -M: LLC "Nedra-Business Center", **2002**. Part 1. 517 p. (in Russ).
- [5] Kishinevsky M.H. // ZhPKh. **1955**. V. 28, No. 9. 927p. (in Russ).
- [6] Kishinevsky M.H. // ZhPKh. **1955**. V. 30, No. 2. 182 p. (in Russ).
- [7] Danckwerts P.V., Sham M. M. // Chem. Eng. 1966. Vd. 44. P. 244-280. (in Eng).
- [8] Danckwerts P.V. Gas-liquid reactions. New York: McGraw-Hill Book Co, **1970**. 276 p (in Eng).
- [9] Zuev AV, Tvardovsky AV // Izv. universities. Chem and chemical technology. **2009**. V. 52, vol. 11. P. 52-55. (in Russ).
- [10] Van Krevelen D.W., Hofstijzer P.J. Kinetics of gas-liquids reactions. Part I. General theory // Rec. Trav. Chim. **1948**. Vol. 67. P. 563-565. (in Eng).
- [11] Van Krevelen D.W. Chem. Eng. Progr. **1948**. Vd. 44, №7. 529p. (in Eng).
- [12] Hitchcock L.B. // Ing. Eng. Chem. **1934**. Vd. 26, №11. 1158p. (in Eng).
- [13] Pozin M.E. // ZhFH. **1947**. V. 20, No. 4. C. 345-353 (in Eng).
- [14] Roper G.H., Hatch T.E., Pigford R.L. // Ing. Eng. Chem. Fundament. **1962**. № 1/2. 144p. (in Eng).
- [15] Faddeenkova GA, Kundo N.N. // ZhPKh. **2003**. V.6, No. 12. S. 1995-1999. (in Russ).
- [16] GOST 23781-87 Gases combustible natural. Chromatographic method for determining the component composition. (in Russ).
- [17] GOST 14920-79 The gas is dry. Method for determining the component composition. (in Russ).
- [18] Kaldybaeva B.M., Dmitriev E.A., Khussanov A.E., Sabyrkhanov D., Abilmagzhanov A.Z. Interphase transfer modeling with simultaneous chemisorption of hydrogen sulfide and carbon dioxide in a chemisorption apparatus // News of the National Academy of Sciences of the Republic of Kazakhstan. Series of Geology and Technical Sciences. Almaty, **2016**. №6. Pp. 219-225. (in Russ). <https://doi.org/10.32014/2018.2518-170X>. (in Russ).
- [19] Kopylov A.Yu., Nasretidinov RG, Vildanov AF, Mazgarov A. Moslovtnoe uptake of hydrogen sulphide and carbon dioxide with a water-alkaline solution // Chemistry and chemical technology. **2010**. V. 53. P.92-96. (in Russ).