



Study of the process of purification of harmful components from gas mixtures by Adsorption

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Abstract

As it is known, the possibility of absorption of gas mixtures by synthetic zeolites is determined by the difference in the shape and size of the molecules of the sorbent substances, therefore it is possible to separate azeotropic mixtures with the help of synthetic zeolites. At the same time, synthetic zeolites lag far behind natural samples in terms of chemical stability and other useful properties. In this regard, the introduction of new types of mineral raw materials, i.e. natural zeolites, into the field of industrial production is considered a special production task and is of great economic importance.

Keywords: acid components; hydrogen sulfide; brew; cleaning; adsorption; desorption, purification of gas mixture

Introduction

In hydrated zeolite crystals, the state of water varies widely from close to the free liquid state to clusters or individual molecules linked to the cations and oxygen of the framework. It depends significantly on the price of the specific volume and dimensions of the voids.

The internal crystalline volume of zeolites and water is 45% of the adsorbent volume. If the structure of the adsorbent is stable, during dehydration, the empty volume of the adsorbent can be filled with molecules of adsorbed substances that generally have one of the chemical properties of zeolites.

The adsorption capacity of zeolite depends on the specific volume determined by the amount of water in the voids of the crystals. Organization of continuous processes of deep separation of gas mixtures in adsorbents is also related to structural and technological difficulties.

A completely new approach has been developed for complete purification of gas mixtures by adsorption in synthetic zeolites [1]. In the adsorption process, especially when separating the components of gas mixtures, it was clarified and determined that the decrease in the adsorption capacity of zeolites is their main drawback. Accordingly, in our example, the size of the pores (as well as grains), the length of the immobile layer, the amount of zeolite adsorbent, and the temperature regime of the adsorption and regeneration stage play a key role for the adsorption of natural gases. The adsorption process of unwanted components of gas mixtures is significantly affected by the rate of passage of gas mixtures through the immobile zeolite layer, which is determined by the difference in bed pressure and the conditions of the considered process for intensive mass exchange.

$$f = \frac{g \Delta P d_e}{2LG^2} \rho; \quad (1)$$

The pressure difference of the formation is determined by the formula (1).

Here, the pressure difference in the immobile layer of Δp -zeolite, Pa: d_e - the equivalent diameter of the particles, ρ - the gas density, kg/m^3 , L - the length of the layer, m , G - the

mass velocity of the gas, kg/sec , μ - the viscosity of the gas, $Puaz$.

Optimum values of the pressure difference in the immobile layer of synthetic zeolite were determined. The optimal value of the pressure difference, which ensures complete absorption of NO_x , varies in a certain range.

The obtained synthetic zeolite was tested. For this purpose, he assembled and experimented with a device as shown in picture 1.

Experimental Part

The use of adsorption methods for the complex processing of low-sulfur gases allows to eliminate gas and sulfur losses and makes it possible to carry out the whole process in a waste-free cycle. The products of the process are a mixture of H_2S and gaseous desulfurized gas. Production waste and gas losses are practically absent. The use of molecular sieves will allow efficient cleaning in the sorption zone at high linear gas velocities, which will allow to significantly reduce the size of adsorbents, as well as to combine the further processing of gas mixtures from H_2S with its deep drying.

Synthetic zeolites IIIaX, IIIaY, CaA, KA were tested in order to choose the optimal adsorbent for purification and separation of gas mixtures from H_2S .

It was found that among the tested adsorbents, the most stable binderless ShaY zeolite in acidic media is ShaX, then CaA. During the experiments, NaA and CaA adsorbents were dispersed the fastest, while NaX adsorbents were dispersed slightly [7].

During the regeneration of zeolite with gas at the temperature of 300-350°C, the colors of zeolites also changed, but at the same time they practically did not undergo surface and structural changes.

During the experiments, a sulfur layer was deposited on the geometric surface of zeolites, but the sulfur layer was removed at temperatures above 350°C. It was determined that after 8-10 adsorption-desorption cycles, the activity of all brands of zeolites in terms of sulfur compounds decreases by 15-20%. Further decline in activity was insignificant.

The desorption of hydrogen sulfide from the tested zeolites at different temperatures was also investigated. At a

desorption temperature below 250°C, the degree of desorption of hydrogen sulfide does not exceed 80% even within 3 hours. It is known that the rate of desorption is closely related to the rate of heat transfer to the zeolite layer (sorber). However, it is not possible to limit the rate of bed temperature increase and, accordingly, to increase the temperature in the desorption zone sharply, thereby reducing the time of H₂S desorption and zeolite reduction. After determining a number of regularities in the adsorption and desorption of sulfur compounds on various zeolites, optimal conditions for adsorption and regeneration of zeolites were selected [3].

Since CO₂ almost always significantly exceeds the amount of hydrogen sulfide in the composition of low-sulfur gases, it is necessary to determine the effect of the presence of CO₂ and H₂S.

To separate gas components from sulfur, adsorbents were used as adsorbents: NaU, CaA, NaA and NaX without binders. The use of synthetic zeolites (up to 20%) caused a number of undesirable side effects: adsorption of high-boiling hydrocarbons and heterocyclic compounds in the secondary porosity of zeolites, low thermal stability, mechanical strength and acid resistance.

It should be noted that in the process of simultaneous adsorption purification of H₂S and CO₂, complete removal of H₂S and CO₂ occurs at the initial time. Then CO₂ is removed from the pores of ShaX zeolite with the help of H₂S [1].

As a result, the amount of H₂S at the outlet of the fixed adsorbent bed increases. Also at this time, H₂S continues to be absorbed until the moment of the jump. By increasing the time of the stage of the adsorption process, it is possible to achieve the desired level of carbon dioxide removal, if H₂S is present in the gas mixture in a high amount, then the adsorption process should be carried out in isothermal conditions.

The method of separation of adsorbates by adsorption in the stationary layer of zeolite-adsorbent is deep absorption of gas mixtures. The products of the adsorption process in a fixed adsorbent bed are a gas mixture purified from all undesirable components and gaseous sulfur. No loss of gas components was detected in the considered process. In this regard, the use of synthetic zeolites of the NaX type will allow to perform fine purification of gas mixtures at high linear gas velocities in the adsorption zone, as well as allow to sufficiently reduce the size of industrial adsorbents and, in particular, the height of the working adsorbent layer. Synthetic CaA, NaA, NaX, and NaY adsorbents were used to select the optimal characteristics of the adsorbent for the deep separation of gas mixtures from CO₂, H₂S, and as a result, it was determined that among the studied zeolites, NaY zeolite is the most profitable in acidic environments, and NaX is the most destructive. is zeolite. The total adsorption capacity of synthetic adsorbent NaX at 250°C is 172 g/l for H₂S.

It was discovered and determined that a significant drawback of adsorbents is their reduced activity in the sorption process, especially during the cleaning of multicomponent mixtures.

While studying the effect of H[^] and CO₂ concentrations on their adsorption by zeolite, it was found that the component composition of substances adsorbed by zeolite depends greatly on the amount of H[^]/CO₂ in the gas.

When the hydrogen sulfide concentration in the raw gas varied from 0.025 to 0.8% by volume, the percentage of hydrogen sulfide in the adsorbate increased from 26 to 60%, while the proportion of adsorbed CO₂ remained almost unchanged. It was also determined that during the regeneration of zeolite, the concentration of hydrogen sulfide in the raw gas was equal to 0.05% of its (hydrogen sulfide) percentage, in the range of 0.2-2.5% in the regeneration gas, and then increased. in the amount of H₂S in gas mixtures up to 3%, in the same conditions its concentration in regeneration gas increases up to 15% by volume.

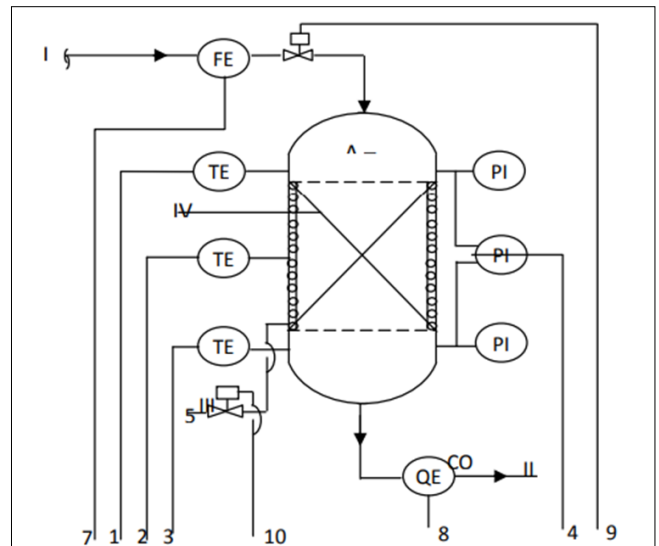


Fig 1: Structural scheme of the process of complete purification of gas mixtures in the immobile layer of the adsorbent by the adsorption method.

A-1-A-4 - adsorber, separator, I - raw material; II - inert gas; III - commodity gas.

It was experimentally determined that complete desorption of moisture requires at least 3 hours. After determining the optimal parameters for the adsorption, desorption and regeneration processes, long-term experiments on the separation of gas mixtures from H₂S by means of an adsorbent were carried out in field conditions.

The rate at which natural gas and gas mixtures pass through a stable adsorbent layer is determined by the formation pressure drop and other conditions necessary for intensive mass transfer, which has a significant effect on the adsorption process.

The process of using zeolites for further purification of gas mixtures from H₂S provides certain economic benefits compared to other adsorption processes under the following conditions:

- When the ratio of CO₂: H₂S exceeds 2.85;
- with a sufficiently large capacity of the installation;
- effectively using zeolite regeneration gases;
- during purification of gas mixtures by adsorption, along with purification from all sulfur compounds (H₂S, CS₂, ZSH).

Zeolite ShaX has greater static and dynamic activity than CaA and NaA zeolites.

Figures 1 and 2 show the kinetic curves of the effect of H₂S and CO₂ [6].

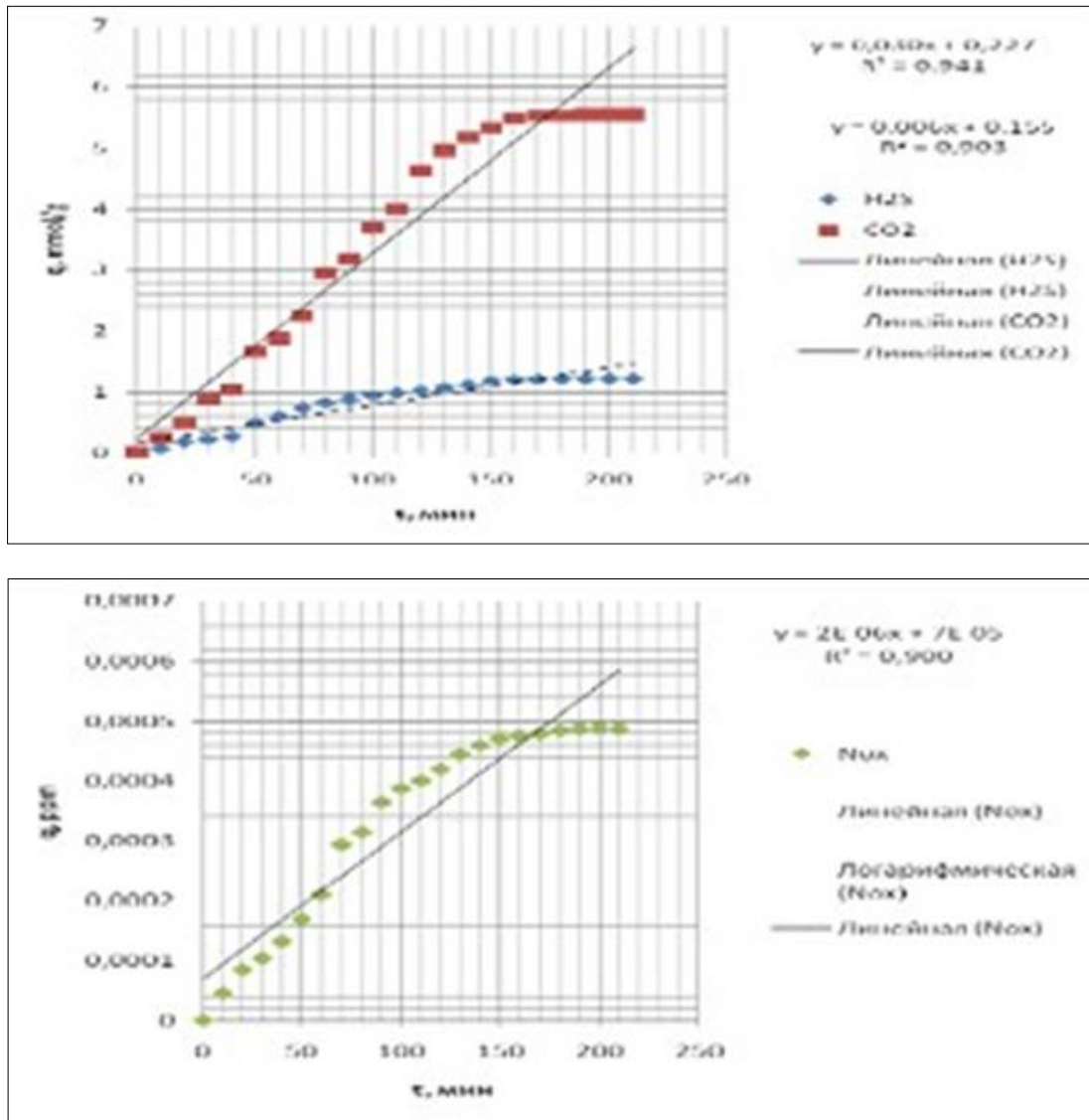


Fig 2: shows adsorption isotherms of CO₂, H₂S and NO₂ from natural gas.

It can be seen from Figure 2 that the equilibrium value of adsorption is different depending on the components. Adsorption isotherms were numerically described by Langmuire equations and the coefficients of the equation were found.

The obtained numerical values of adsorption isotherms of CO₂, H₂S and NO₂ from gas mixtures can be used for mathematical modeling of this process in the future.

Depending on the conditions of the adsorption process, the concentration values of the gases in the purified flow at the adsorber outlet are shown in table 1.

The different values of diffusion coefficients obtained are shown in Tables 2 and 3. Apparently, they depend significantly on the initial adsorbent concentration, adsorption temperature and pressure drop in the fixed zeolite bed.

Their dependence is approximated by equations for each component separately:

The coefficients of the equation (2), (3), (4) were calculated with the help of the "Matlab" program.

Table 1: Values of the concentration of gases in the purified stream at the adsorber outlet depending on the conditions of the adsorption process.

The value of the pressure difference in the adsorption layer, kg / cm ²	The composition of the components of gas mixtures after purification in % volume		
	H ₂ S	CO ₂	NO ₂
0,151	0,58	0,42	0,88
0,161	0,55	0,32	0,79
0,169	0,48	0,19	0,69
0,181	0,43	0,13	0,061
10,183	0,41	0,12	0,060
0,198	0,42	0,103	0,068
0,216	0,43	0,15	0,075
0,231	0,44	0,22	0,085
0,241	0,48	0,27	0,093

Table 2: Values of diffusion coefficients at different temperatures for the H₂S component

№	τ ₀ min	The temperature of adsorption °C		
		-10	25	45
Diffusion coefficients ($D_m \cdot 10^{15} \text{ sm}^2/\text{min}$)				
1	20	151	133	125
2	40	140	121	115
3	60	119	98	93
4	80	98	83	75
5	100	81	71	63
6	120	67	56	48
7	140	43	40	32
8	160	24	26	18
9	180	13	12	10
10	200	7	5	4

Table 3: Values of pressure gradient and time-dependent diffusion coefficients in the fixed bed of zeolite

№	τ, min	Pressure gradient ΔP in the immobile layer of zeolite											
		15	16	17	18	19	20	21	22	23	24	25	26
Diffusion coefficients ($D_m \cdot 10^{15} \text{ sm}^2/\text{min}$)													
1	20	111	117	125	132	143	148	161	173	190	198	201	207
2	40	98	102	115	118	122	112	148	161	177	183	193	198
3	60	72	74	85	89	94	98	112	138	154	168	179	184
4	80	58	61	64	65	67	66	71	80	98	100	133	138
5	100	41	44	47	51	51	55	57	63	74	92	122	132
6	120	32	34	35	39	38	42	41	50	69	73	95	99
7	140	24	28	29	30	32	33	32	36	45	62	76	82
8	160	18	18	21	22	24	25	26	28	32	33	47	51
9	180	6	7	7	11	18	18	21	22	24	25	28	30
10	200	4	6	5	7	8	7	7	9	8	12	14	15

Thus, the proposed gas mixture separation method is three-component, using zeolite, maintaining a pressure difference of 0.173 - 0.203 kg/cm² in the adsorption layer, the initial composition of which corresponds to H₂S - 80%, CO₂ - 15%, NO_x - 5%. allows adsorption relative to the gas mixture.

The optimal conditions for the adsorption process of the gas components in the mixture is to carry out the process at a pressure difference of 0.193 kg/cm² in the adsorption layer, which ensures the composition of H₂S - 0.40, CO₂ - 0.10, NO_x - 0.061 after purification.

Previously, the degree of non-utilization of adsorption capacity in various zeolites was Na X - 49%, Na A - 42%, CaA - 23%].

The conducted experimental work shows that when the gas velocity is 1.5 m/s and the pressure difference is 0.173-0.203 kg/cm² in the adsorption layer, the degree of underutilization of the adsorption capacity approaches zero.

The method of purification of gas mixtures containing carbon dioxide, nitrogen dioxide and hydrogen sulfide, which includes the contact of the gas stream with NaX synthetic zeolite, is distinguished by the fact that the process is carried out at a pressure difference of 0.173 - 0.203 kg/cm² in the adsorption layer.

The method of purification of gas mixtures from unwanted components refers to gas processing, in particular, to the method of adsorption purification of natural gases with the help of synthetic adsorbents. This method is used in gas processing, oil refining and petrochemical enterprises.

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