UTILIZATION OF ZEOLITE WASTE FOR USE IN THE ADSORPTION TREATMENT OF NATURAL GASES

Makhamadjanov Makhamat-Ibrakhim Akhmatjanovich
Candidate of Technical Sciences, associate professor, Tashkent State Transport University, Uzbekistan
Alimova Zebo Xamidullaevna
Candidate of Technical Sciences, professor, Tashkent State Transport University, Uzbekistan
Magdiev Karimulla Irgashevich
Senior Lecturer, Tashkent State Transport University, Uzbekistan
https://doi.org/10.5281/zenodo.7384742

Annotation.
The purpose of this work is to study the utilization of zeolite waste for use in the adsorption purification of natural gasesand their effect on the adsorption-desorption characteristics in natural gas desulfurization processes for the purpose of their secondary use in desulfurization processes.
Keywords: adsorption, zeolite waste, desulfurization, natural gas, desorption characteristics.

Introduction.

Natural gases extracted from the largest deposits of Uzbekistan (Shurtan, Mubarek, etc.) are low-sulfur. Therefore, the purification of these gases from hydrogen sulfide (H2S) at gas processing plants is carried out by adsorption using synthetic zeolites. Synthetic zeolites are imported to our Republic from abroad (USA, Germany, France, Japan, Austria, etc.) for foreign currency at the price of the world market. These zeolites, during long-term operation in adsorption-desorption cycles, gradually lose their properties, become unusable and are disposed of as industrial waste.

The applied technology of adsorption purification of natural gas from hydrogen sulfide in the gas fields of the Republic, based on the use of these imported zeolites, requires significant foreign exchange costs associated with the annual emission of thousands of tons of spent zeolites in the form of waste.

Therefore, the issue of extending the service life of imported zeolites, i.e. restoring the original properties of spent zeolites and their secondary use in gas processing is of urgent importance.

Research methodology.

The purpose of this work is to study the degree and structure of contamination of spent zeolites and their effect on adsorption-desorption characteristics in natural gas desulfurization processes, to determine the number and structure of zeolite transport pores and their role in the adsorption process, to develop an optimal method for the recovery of zeolite waste for their secondary use in desulfurization processes.

In solving the above problems, the methods of physical chemistry, quantitative and qualitative analysis of pollution products, the theory of redox reactions of the gorenje process, methods of calculating mass-heat exchange processes are used in the work.

The study of the composition of spent zeolites showed that during long-term operation of zeolites in adsorption-desorption cycles at industrial natural gas desulfurization plants, they are contaminated with oxidation-reduction reaction products (hydrocarbon, hydrogen sulfide, carbon dioxide and water vapor) contained in raw gas, which leads to the deposition

of these products on the zeolite surface and a sharp narrowing transport pores, and this, in turn, leads to a decrease in the dynamic activity of the zeolite.

Depending on the service life of zeolites and the composition of gas (especially containing heavy hydrocarbons), the amount of pollution products ranges from 2% to 4% and the dynamic activity decreases by 40-50%, which makes their further use impractical, and currently zeolites have not been used in desulfurization plants for more than 3 years.

The following table shows the results of laboratory studies to determine the degree of contamination of various imported synthetic zeolites, depending on their service life (Table 1.).

Table 1.

Contamination of zeolites depending on the service life

Service life Brand of zeolite	Degree of contamination, in %							
	1 month		12 months		18 months		24 months	
NaA (4A) (USA)	0,135 0,137 0,136	0,136	1,47 1,42 1,45	1,44	2,17 2,20 2,15	2,17	2,94 2,91 2,86	2,9
CaA (5A) (USA)	0,139 0,133 0,136	0,136	1,52 1,46 1,50	1,49	2,25 2,21 2,23	2,23	2,97 3,02 2,94	2,97
Seca (France)	0,131 0,126 0,130	0,129			2,12 2,07 2,11	2,10	2,85 2,91 2,77	2,81
Bitterfeld (Germany)	0,145 0,142 0,143	0,143					3,08 3,10 3,15	3,11

The structure of contaminants and their adsorption properties of zeolites were determined by changes in the kinetic and dynamic properties of adsorbents.

It is known that the main characteristic of adsorbents is their absorption capacity, i.e. the degree of gas purification during adsorption. The absorption capacity of the spent zeolites was determined by removing the adsorption isotherms on a device, the principle of operation of which is based on measuring the change in gas pressure during adsorption at a constant volume. Figure 1 shows the isotherms of H2S adsorption on spent and fresh zeolites, from which it can be seen that the service life of zeolites in desulfurization plants has almost no effect on the adsorption isotherms. This indicates that with multiple adsorption-desorption cycles of gas purification, only the transport pores of zeolites are polluted, and the adsorption cavities are practically not exposed to contamination.

To study the dynamic characteristics of spent zeolites, depending on the service life, tests were carried out on a pilot plant.

The test results are shown in Table 2, which shows the effect of the service life of zeolites on their dynamic activity.

Table 2.

Service life Brand of zeolite	Dynamiccapacity, in %					
	Fresh zeolite	1 month	14 months	15 months	21 months	24 months
Bitterfeld (Germany)	1,4	1,38				0,76
CaA (5A) (USA)	1,2	1,16			0,58	
NaA (4A) (USA)	1,2	1,14		0,61		
Seca (France)	1,1	1,09	0,62			

The process of zeolite reduction, i.e. oxidation of pollution products, occurs with the release of a significant amount of heat.

To carry out this reaction, a sufficiently high temperature is required (400-4500C), but at the same time, due to the thermal effect of the reaction, the temperature of the adsorbent layers can overheat by another 150-2000 C.

To prevent such overheating, a reagent was used, which decomposes endothermically under the conditions of zeolite reduction and allows to regulate the temperature of the oxidative reaction to a certain extent. Ammonium nitrate (NH4NO3) was used as a reagent, which decomposes at a temperature of about 4500 C with heat absorption, which prevents overheating of the adsorbent surface.

With this method of restoration, the zeolite completely acquires its original properties. The appearance changes from gray to white or yellowish, i.e. it takes on its original appearance.

The results show that this method of recovery is considered more effective than the previous ones, and the degree of recovery reaches 100% or more. This is apparently due to a certain expansion of the transport pores due to some dissolution of the zeolite binding materials. However, it should be noted that the mechanical characteristics of zeolite granules deteriorate somewhat. In addition, the recovery technology requires additional costs for ammonium nitrate, distilled water, and the energy costs associated with the pre-drying of zeolite will increase.

Based on the results of laboratory studies aimed at finding the optimal mode of recovery of zeolite waste and a feasibility study of the recovery method, it was possible to abandon the preliminary promotion. Table 3 shows the test results.

Table 3

Test results

Type of adsorbent	Dynamic capacityafter recovery	% recovery
Spent zeoliteBitterfeld (Germany)	0,78	
Reconstituted zeolite Bitterfeld (Germany)	1,38	98,5
Fresh imported zeolite Bitterfeld (Germany)	1,4	
Spent zeolite CaA (5A)	0,58	
Reconstituted zeolite CaA	1,18	98,3

Fresh imported zeolite Bitterfeld CaA	1,2	

During the long-term operation of zeolites in the adsorption–desorption cycles of desulfurization plants, they are contaminated with oxidation-reduction reaction products contained in crude gas (hydrocarbons, hydrogen sulfide, carbon dioxide and water vapor), which leads to a sharp narrowing of transport pores, resulting in a decrease in its dynamic activity.

As a result of studying the kinetics of hydrogen sulfide adsorption on spent and recovered zeolites and using the mathematical apparatus of the theory of mass transfer, a method for determining the structure of transport pores was developed and a change in the dynamic characteristics of zeolites from the narrowing of the capillary size as a result of contamination was revealed.

References:

1.Mahamajanov, M. I. A., Alimova, Z. H., &Magdiev, K. E. (2022). Recovery of zeolite waste for reuse in the purification of natural gases. European Journal of Interdisciplinary Research and Development, 8, 1-4.

2.Alikaev R.S. Drying and purification of natural gas from hydrogen sulfide and carbon dioxide impurities on exchange forms of granular zeolites A and X without binders. Dissertation for the degree of Candidate of Technical Sciences. Ufa. 2012.

3.IbragimovCh.Sh., Babaev A.I. Scientific foundations and practical tasks of chemical cybernetics. Baku. AGNA Publishing House, 2015.

4.Arutyunov V.S. et al. Technology of processing of hydrocarbon gases. Textbook for universities. Moscow, Yurayt Publishing House, 2020.p.-723.