REGENERATION OF ZEOLITE FOR RE-USE IN NATURAL GAS PURIFICATION

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Abstract. *The purpose of this work is to study the degree and structure of contamination of spent zeolites and their impact 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 in order to reuse in desulfurization processes.*

Keywords: *adsorption, zeolite waste, desulfurization, natural gas, desorption characteristics.*

INTRODUCTION

Modern scientific and technological progress is associated with the constant acceleration of the consumption of natural resources and the development of production.

The current situation regarding the consumption of raw materials is delayed due to the uncontrollable increase in the amount of waste. A large amount of it enters the atmosphere in the form of dust and gas waste, water bodies along with wastewater and soil, which has a very negative effect on the environment.

However, the current level of use and processing of primary and secondary resources significantly lags behind the tasks of increasing the efficiency of social production. The Republic of Uzbekistan, having its own potential subsoil resources, due to their slow involvement in economic circulation, is forced to import a number of industrial materials and reagents, including expensive synthetic zeolites for gas processing, which are discarded as waste after operation. Therefore, the question of extending the service life of imported zeolites, i.e. restoration of the original properties of spent zeolites and their secondary use in gas processing is of current importance.

The purpose of this work is to study the degree and structure of contamination of spent zeolites and their impact 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 the purpose of their recycling in desulfurization processes.

To solve the above problems, the work used methods of physical chemistry, quantitative and qualitative analysis of pollution products, the theory of redox reactions of the combustion process, and methods for calculating mass and heat transfer processes.

A study of the composition of spent zeolites showed that during long-term operation of zeolites in adsorption-desorption cycles in industrial natural gas desulfurization plants, they become polluted with oxidation-reduction reaction products (hydrocarbon, hydrogen sulfide, carbon dioxide and water vapor) contained in the raw gas, which leads to to the deposition of these products on the zeolite surface and a sharp narrowing of transport pores, and this, in turn, to a decrease in the dynamic activity of the zeolite.

Depending on the service life of the zeolites and the composition of the gas (especially those 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 in desulfurization plants are more 3 years have not been used.

The table below 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 service life

Life time, Zeolite grades	Degree of pollution, %							
	1 month		12 month		18 month		24 month	
CaA (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 the adsorbents.

It is known that the main characteristic of adsorbents is their absorption capacity, i.e., the degree of gas purification during the adsorption process. The absorption capacity of spent zeolites was determined by taking adsorption isotherms on a device whose operating principle is based on measuring the change in gas pressure during the adsorption process at a constant volume. The service life of zeolites in desulfurization plants has almost no effect on 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 as a function of service life, tests were carried out in a pilot plant.

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

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

$$CxHyS_2 + O_2 \rightarrow CO_2 + SO_2 + H_2O + Q$$

To carry out this reaction, a sufficiently high temperature is required (400-450 ºC), but at the same time, due to the thermal effect of the reaction, the temperature of the adsorbent layers can overheat by another 150-200 ºC. To prevent such overheating, a reagent was used, which, under the conditions of zeolite reduction, decomposes endothermically and, to a certain extent, makes it possible to regulate the temperature of the oxidation reaction. Ammonium nitrate (NH_4NO_3) was used as a reagent, which decomposes at a temperature of about 450 ºC with the absorption of heat, which prevents overheating of the adsorbent surface.

$$NH_4NO_3 \rightarrow NH_3 + NO_2 + H_2O - Q$$

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

Table 2

Life time, Zeolite grades	Degree of pollution, %					
	Fresh zeolite	1 month	14 month	15 month	21 month	24 month
Биттерфельд (ФРГ)	1.4	1.38				0.76
CaA (5A) (США)	1.2	1.16			0.58	
Na (4A) (США)	1.2	1.14		0.61		
Сека (Франция)	1.1	1.09	0.62			

The results show that this recovery method is considered more effective than previous ones, and the recovery rate reaches 100% or more. This occurs, 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 in this case the mechanical characteristics of the zeolite granules deteriorate somewhat. In addition, the recovery technology requires additional costs for ammonium nitrate, distilled water, and the energy costs associated with pre-drying of the zeolite will increase.

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

Table 3

Type of adsorbent	Dynamic capacity after recovery	% recovery
Spent zeolite "Bitterfeld"	0.78	
Reduced zeolite "Bitterfeld"	1.38	98.5
Свежий импортный цеолит «Биттерфельд»	1.4	
Spent zeolite CaA (5A)	0.58	
Reduced zeolite CaA	1.18	98.3
Fresh imported zeolite CaA	1.2	

CONCLUSION

During long-term operation of zeolites in adsorption-desorption cycles of desulfurization installations, they become contaminated with oxidation-reduction reaction products contained in raw 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.

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

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

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