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Drying and Purification of Natural Gas on Modified Clinoptilolite Type Zeolite by Adsorption Method

Abstract

Adsorption properties of sulfurous compounds in natural gases have been studied using clinoptilolite type zeolite catalyst with rich deposits in Azerbaijan. As a result, it was determined that the use of modified clinoptilolite is the most effective based on experimental evidence for the adsorption of H_2S, COS and RSH on modified clinoptilolite and NaX zeolite. Based on H_2S and COS adsorption heats in modified clinoptilolite, the optimal temperature of regeneration was determined at 250 °C. This is the value of the rate of desorption of sulfur compounds (H_2S and COS) from NaX zeolite at 320 °C, determined in industry, in other equal conditions. Thermally modified clinoptilolite is shown to have the best absorption and protective properties.

Keywords: *sulfurous compounds, adsorbent, natural zeolites, modification, clinoptilolite, mordenite*

Introduction

Currently, there are various methods of extracting sulfur compounds (H_2S və COS) in the industry. Among them, adsorption processes occupy an important place. Synthetic and natural zeolites are most often used as adsorbents, they differ in polar molecules and have a high absorption capacity at low concentrations. The price of natural zeolites is very low, they are resistant to high temperatures and aggressive environments. Among natural zeolites, clinoptilolite is of the greatest interest.

Taking this into account, the adsorption properties of sulfur compounds contained in natural gases were studied in Azerbaijan using a clinoptilolite type zeolite catalyst with rich deposits. Of the several dozen mineral types of zeolite in Azerbaijan, only clinoptilolite, mordenite, shabazite and phillipsite are of practical importance.

For some consumers (adsorption technologies, production of catalysts, etc.) in most cases, modification of zeolites produced by solutions of acids, alkalis, salts or other substances is required. Other types of modifications are also used: phosphorus, arsenic, volatile organic compounds, quadruple chloride hydrocarbon, silica compounds, hydrogen sulfides, etc.

It should be noted that chemical methods of processing zeolites have a number of significant disadvantages. The thing is that any chemical treatment of zeolites affects many chemical elements, including those with biological value. After chemical treatment of a certain zeolite rock with a prohibited set of micro- and macroelements, the mechanism of its action is significantly disrupted. The positive side of the chemical treatment of terraformed rocks with zeolite is that, when used, it is possible to change the properties of zeolites in the desired direction. Therefore, the use of such technologies makes it possible to significantly expand the scope of application of zeolite-containing rocks.

In modern conditions, the production of zeolite products of the required quality can be achieved not only by chemical, but also by mechanical and physical action. It should be noted that the prospects for the widespread introduction of natural zeolites into the national economy are mainly related to the problems of obtaining marketable products from the mature mass of zeolite-containing date sauces that meet the requirements of consumer sectors.

When using zeolites in most sectors of the national economy, the following main water-alluvial ones are formed: removal of polluting additives; an increase in the amount of zeolite in the commercial product compared to the original rock; improve the performance of any class of materials.

The capabilities of most of the main products-OTI-to produce high-quality zeolite products have been investigated using enrichment methods using structural differences in particle size, density, hardness, magnetic susceptibility, wettability and other characteristics of the components being separated. In the processing of zeolites, gradient enrichment, magnetic and electrostatic separation, flotation, as well as chemical treatment aimed at changing the substance are used.

Clinoptilolite is a layered zeolite discovered by Schaller and belonging to the mordenite group (Mina, 2019). According to various researchers, the size of the access windows to the intracrystalline spaces of clinokyrolite is 3.5 – 4.4.

According to their chemical composition, three main groups of clinoptilolites can be distinguished: with a predominance of Ca^{+2} cations (Shuts, Rhodopa, Balkhash, Dzegvi, Novi-Kochb deposits); with a Na^+ cation (Cermine deposit); with a predominance of K^+ cations (deposits in Italy, Patagonia). At the same time, for some types of clinoptilolite, a high content of two cations was obtained, for example, for cuneiform tyrolite of the Shuts deposit-the presence of calcium and potassium cations, for cuneiform tyrolite of the Balkhyz deposit-the presence of calcium and sodium cations.

Table 1 presents the comparative mineralogical composition of zeolites, which are the most typical deposits in different countries.

Table 1.
Mineralogical composition of zeolites

Minerals	**Deposits**			
	Aydag	Dzegai	New Kohob	Bakiz
Clinoptilolite	77-85	85-95	85-95	71-76
Quartz	15-18	1,5-2,5	5,0-7,0	17-25
Calcite	1,8-2,5	0,85	0,48	1,2-3,0
Biotite and chlorite	2,0-4,0	3,0-4,0	3,5-5,0	1,5-3,5
Other minerals	2,0-2,5	1,5-3,2	0,6-2,0	2,0-3,0

Although the order of selectivity varies slightly, a similar pattern is generally preserved for Salt alloys: $Rb^+ > Li^+ > K^+ > Na^+$ (Sharipov, 2016, p. 267-269). The indicated property of clinoptilolites makes it possible to use them as ion exchange materials in the processes of purification of tap water at industrial enterprises and other sectors of the national economy.

Granulation of small fractions in cuneiform-montmorillonite rocks allows, with the help of sorption processes, to increase the fractional yield to the required values from -5 to +3 mm, and the fractional output from -3 to +1 mm can be adjusted.

The highest concentration of a whole component-clinoptilolite-falls on the fraction $p = 2.14\text{-}2.20$ g/cm^3, and the maximum content is recorded in multiples of $p = 2.16\text{-}2.205$ g/cm^3. In the fraction $P = 2.205$ g/cm^3 and in layers of higher density, the insignificant content of quartz is noted, which is explained by its presence in a fine compound with other minerals. Starting from a layer of $P = 2.210$ g/cm^3, cuneiform thyrite predominates in fractions, the content of which in the sample increases to a noticeable $p = 2.230$ g/cm^3. In addition, they are intensively enriched with quartz as the density of the fractions increases.

Studies point to the possibility of gravitational release of the enriched polevoshpat group of clay mineral, cuneiform concentrate and quartz fractions enriched with a heavier mineral.

However, the main disadvantage of this method is the use of zeolites as a means of separating the compound of organic bromoform and dimethylformamide liquids from absolute absorbable, and their further desorption is extremely difficult from a technical point of view.

Thus, achieving an efficient separation of zeolite minerals (cuneiform tyrolite), clay particles and minerals of the feldspar and quartz group significantly violates the technological properties of zeolites.

In connection with the acquisition of clinoptilolite concentrates, a gravitational magnetic plating scheme was developed. Thus, studies have proposed a laboratory scheme for the isolation of clinoptilolite concentrates for one of the types of zeolite-containing rocks of the Aydag deposit (rich in clinoptilolite and weak montmorillonite), determined that the yield of the Hashed clinoptilolite concentrate can potentially be 75-80 %, while the amount of clinoptilolite is about 90-95 %. In this case, the montmorillonite part si remains in the zeolite concentrate.

Each branch of the national economy manifests itself as an influencer on the quality of zeolite raw materials obtained by chemical, physical and complex influences. At the same time, modern technologies for processing and plating zeolite-containing rocks do not always allow obtaining zeolite products of the required quality.

Of great importance in the number of sorption-regeneration cycles, as well as in the process of functioning of natural zeolites as adsorbents of one purpose or another, there is a regeneration process. It is most profitable both economically and environmentally – do not throw away natural zeolites as long as possible and do not extend the service life. Thus, the issue of industrial application of natural zeolites as adsorbents is positively solved by an effective method of their regeneration.

In this situation, during the use of natural seolites, the recovery of the adsorbent The problem of geo-chemical barriers, the release of pollutants Cleaning of hot water, fuel and energy production waste gases It occupies an important place in you. As a rule, the use of natural seolites as adsorbents is proposed in this or other industry. It is the level of regulation that determines the quality of the sound.

The main property of clinoptilolite as an adsorbent is its ability to absorb moisture. Mu is the amount of water in the voids in the crystals. The moisture content of clay is highly dependent on its cationic form.

The increase in the atomic mass of the metal in the same valence Falling down with heat. This is due to the increase in the volume of the particles and the decrease of the free volume in the cell of the zeolite. As the charge density of the second cation decreases, the rate of hydration is related to its decrease (Mazgarov, 2015, p. 70).

Compared to synthetic zeolites of type A and X, clinoptilolite is smaller in size. It has a larger volume and is easier to water. Clinoptilolite already loses 80.3 % of its original amount of water at a temperature of 200 °C. In the same conditions, NaA and NaX lose 50 % and 57 % of water, respectively.

Clinoptilolite well adsorbs substances whose molecules are small in size (no larger than 4 Å): water, carbon dioxide, oxygen, nitrogen, etc. (Nikiforov, 2011, p. 48; Savostyanov, 2014, p. 43-48). In clinoptilolit, the adsorption isotherms of water vapor have a steep rise in the initial section, which is kharakhterik for microporous adsorbents. At a relative pressure $P/Ps=0.1-0.2$, the voids of the clinoptilolite are almost completely filled with water.

The properties of natural clinoptilolite are shown in Table 2.

Table 2.
Properties of natural clinoptilolite

Indicator	Clinoptilolite
Bulk density: g/cm^3	0.65 – 0.7
Clinoptilolite content: without less %	76 – 80
Porosity: %	29.4 – 50
Granular porosity: at least %	40
Water resistance: at least %	95
Vibration wear: without less %	1
Heat resistance: ^{0}C	650
Mechanical crushing strength of granules: at least	8 kg per pellet
Exchange capacity for NH_4: at least mg-ekv/g	0.70 – 2.5
Standard fractions: output of target fraction at least 85 %	3 – 5 mm
Moisture capacity in static conditions at relative humidity (1.0 %): at least	60 mg/sm^3
Appearance:	irregularly shaped granules
Color:	light gray, yellow gray
The dimensions of the windows, Å	4.0 – 7.2

The most common methods for cleaning natural gas from hydrogen sulfide are chemosorption processes. Aqueous solutions of alkali metal salts of organic bases – amines: carbon, phosphoric acids, amino acids are widely used as reagents in this group of processes (Seong, 2011, p. 583-590).

The regeneration of the saturated solution is carried out by boiling it in a reboiler heated by steam or flame at a temperature of 70-150 °C. Sour gases from the regeneration are sent to the production of sulfuric acid or elemental sulfur by the Klaus method. When the gas contains carbon dioxide, it is removed together with hydrogen sulfide. But the absorption rate of CO_2 is much lower than the absorption rate of H_2S. This allows, in cases where the amount of carbon dioxide in the purified gas is not regulated, to regulate its absorption in the purification process and thereby reduce energy costs. The absorption selectivity of H_2S for primary and secondary amines, which interact with CO_2 to form carbonates, is very low. This reaction belongs to the class of fast reactions. The selectivity of H_2S absorption decreases with increasing absorption temperature and irrigation density.

The degree of purification of gas from sulfurous organic compounds in the processes under consideration is generally not higher than 30 %. Mercaptans and carbon disulfide are absorbed mainly at the expense of physical solubility. The removal of carbonyl sulfide is determined by the rate of its hydrolysis in an alkaline solution and increases with the rise of the pH of the solution. The optimum processing temperature is 60-80 °C.

The ability of aqueous solutions of chemosorbents to absorb acid components practically does not depend on the partial pressure of acidic components in the gas phase, being a function of temperature and the amount of chemosorbent. For this reason, when the amount of sulfurous compounds in the purified gas increases, the energy costs of circulating the absorbent solution in the system and its regeneration increase almost proportionally. To lower the amount of hydrocarbons in sour gases, multi-stage aeration of the saturated absorbent is applied, followed by compression of the aeration gases and their return to the purification cycle, as a result of which energy costs are significantly increased.

Physical absorption processes are more economical than amines if the partial pressure of acidic components in the purified gas exceeds 4-6 atm, depending on the type of organic solvent.

Physico-chemical absorbers, consisting of a mixture of amines, physical solvents and water, are characterized by a high degree of absorption of sulfur compounds and CO_2 in the area of both high and low partial pressure. The effect of physico-chemical absorbers is based on chemosorption of CO_2 and H_2S with amines and physical solubility of sulfurous organic compounds.

However, the initial quality of zeolite-containing rocks of these deposits does not always satisfy the need for this type of raw materials in the oil and gas industry, agriculture and animal husbandry, as well as in medicine, food industry, etc. its requirements for the content of zeolites and various types of impurities for use (quartz, iron oxides, etc.).

For example, when using natural zeolites as bioactive additives, extremely stringent requirements are imposed on the iron oxides contained in them, the use of zeolites in most medical fields requires their monomineralityy, and the requirements for the purity of zeolite products for livestock and fish farming are tightened. The gas processing industry also strictly regulates the quality of zeolites, the main requirement is that the content of zeolite should be from 90 to 100 %.

In this regard, there is a need to develop technology for processing and enriching zeolite-containing rocks, which can provide the necessary purity of zeolites and obtain high-quality commodity products that meet the conditions of one or another branch of the national economy (Angelova, 2011, p. 306-311).

However, at present, the issues of deep enrichment of zeolite-containing rocks are at the initial stage of development. In industrial conditions, the preparation of zeolites for use in the national economy is limited to decomposition and threshing in several stages. Large-sized raw materials are first crushed, and then crushed in 2-3 stages.

Sometimes the primary processing scheme includes additional drying, tabletting or granulation of crushed material by crushing. A type of zeolite divided into fractions is a catysh product sent directly to consumers. In industrial use, all fractions of zeolite raw materials are applied up to 10 mkm 4 mm.

In Azerbaijan, seolite has a number of minerals, mainly clinoptilolite, mordenite, shabazite and phylipsite, which make up the practical population.

It should be noted that chemical processing methods zeolites have a number of significant drawbacks. The thing is that any chemical processing of zeolites affects many chemical elements, including biologically valuable ones. After chemical processing of a certain zeolite rock with a ban-gilt set of micro – and macroelements, the mechanism of its action is significantly distorted. The positive side of the chemical processing of zeolite-containing rocks is that during its application it is possible to change the properties of zeolites even in the required direction. Therefore, the use of such technologies can significantly expand the area of geolith-containing rocks.

In modern conditions, the production of zeolite products of the required quality can be achieved not only by chemical, but also by mechanical and physical influences.

It should be noted that the prospects for the widespread use of natural zeolites in the national economy are largely associated with the problems of purchasing products for sale from the sexual mass of zeolite-containing rocks that meet the requirements of consumer industries (Garcia-Basabe, 2010, p. 187-196).

Based on the results of experimental tests, the expediency of using modified clinoptilolite in desulfurization processes in combination with synthetic zeolites is revealed: the first layer of synthetic zeolite along the purified gas flow, the complementary layer – clinoptilolite. Since the adsorbent processing rate in complementary layers is low, replacing synthetic zeolite with clinoptilolite will not have a noticeable effect on the total sulfur capacity of the layer. On the other hand, taking into account the high thermochemical durability of clinoptilolite and its low catalytic activity in cracking reactions, the use of a combined layer in reverse-flow regeneration will allow to increase the service life of adsorbents (Rakitskaya, 2014, p. 52-58).

Currently, adsorption methods in the presence of various solid adsorbents are used to purify low-sulfur gases at high concentrations of carbon dioxide. These processes take advantage of the high selectivity of zeolites. For example, hydrogen sulfide is better adsorbed than a mixture of nonpolar gas and liquid coal hydrogens.

The processing of low-sulfur gases at high concentrations of carbon dioxide has a great effect taking into account the properties and characteristics of the low-sulfur gases, the zeolite surface A new way of cleaning by adsorbing in water, then desorbed hydro The catalytic conversion of gen sulphide to elemental sulfur is determined.

The use of adsorption method for complex processing of low-sulfur gases, gas and sulfur It allows us to eliminate someone and leads the whole process to a period without jumping. The gas mixture and gas sulfur products of the process are cleaned of H_2S. Production waste and gas loss are almost non-existent. The use of molecular sieves will allow efficient purification in the sorption zone at a high linear gas velocity, which will allow to significantly reduce the size of adsorbers, as well as to combine the purification of gas mixtures from H_2S with deep drying (Yusubov, 2016, p. 22-23).

Synthetic zeolites are much lower than natural samples in terms of chemical stability and other useful properties. In this regard, the study of new types of mineral raw materials, that is, natural zeolites, is one of the important national economic tasks and has great economic importance (Adzhiev 2017, p. 43-48; Makhmudova, 2019, p. 159-166).

Due to the presence of industrial deposits of natural zeolite, Azerbaijan can be represented as one of the large zeolite regions of the CIS, which can provide the national economy with the necessary raw materials for decades to come.

Conclusion

Based on experimental data on adsorption of H_2S, COS and RSH in modified clinoptilolite and NaX zeolite, the concentration range of sulfur compounds in which the use of modified clinoptilolite is most effective was determined. Depending on the temperature, an increase in the adsorption capacity of modified clinoptilolite due to ethyl mercaptan was recorded, which is explained by the appearance of a sieve effect. Based on this, it was concluded that the use of modified clinoptilolite for purification of natural gases from ethylmercaptan is advisable in cases where further gas processing is carried out at high temperatures.

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