Study of sorption properties of HF 512O and NaX synthetic zeolites in the process of sorption of air mixture components

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Abstract. The sorption properties of synthetic zeolites HF 512O and NaX were studied. In the course of the study, the volume method obtained the sorption capacities of zeolites for nitrogen and oxygen. The experimental setup for determining the sorption capacity by volumetric method consisted of two tanks. The first tank has a known volume, and the second tank is filled with the studied sorbent. Helium was used to determine the free volume of the second tank. The gas sorption capacity of which must be determined is fed to the first tank, the second tank is pumped out using a vacuum pump, after which the tanks are connected and the separation in the tanks is leveled. Thus, the sorption capacity of the sorbent can be calculated based on the pressure drop in the system. The selectivity of sorbents for the nitrogen–oxygen pair for pure gases was calculated.

1. Introduction
Currently, three main separation technologies are used to obtain oxygen by air separation [1]: membrane, sorption, and cryogenic. The applicability of a particular technology is most often due to the amount of oxygen that needs to be produced [2]. Each method has its own advantages and disadvantages [3].

The most cost-effective method for obtaining oxygen is the cryogenic method, which allows obtaining air components in almost unlimited quantities [4]. The energy consumption in this case, depending on the size and scheme, is up to 1.6 kWh per 1 cubic meter of oxygen [4]. The technology is based on air liquefaction and its subsequent separation by low-temperature rectification. Thus, the separation process is carried out at very low temperatures. Equipment for implementing the cryogenic method is quite cumbersome and takes up a lot of space. In addition, only specially trained personnel can use cryogenic installations due to their hardware complexity.

The adsorption separation method is based on the adsorption process. The adsorption process consists in the difference in the sorption capacities of the adsorbents with respect to the components of the shared mixture and the difference in the rate of sorption of the components [5]. In other words, one or several components of the mixture to be separated are selectively absorbed by the surface of the solid adsorbent [6], which are most commonly used zeolites for air separation [7]. In this case, the sorption capacity depends on the temperature and pressure at which the process proceeds. Pressure Swing Adsorption (PSA) is based on a cyclic process of adsorption-desorption at different pressures [8]. Depending on what pressure is carried out adsorption and desorption of the PSA installation can be divided into the following types [9]: PSA pressure at which the pressure above atmospheric adsorption, and desorption occurs at atmospheric pressure, VSA (Vacuum Swing Adsorption) [10] in which adsorption occurs at atmospheric pressure, and desorption in vacuum and vacuum-pressure VPSA (Vacuum Pressure Swing...
Adsorption) [9] in which adsorption occurs at pressures above atmospheric, and desorption under vacuum [11].

Membrane separation is based on different rates of penetration of molecules of separated gases through the membrane under the action of a driving force [12]. The prospects for using membrane technology in gas separation are determined primarily by the simplicity of the process design, cost-effectiveness, long-term operation of gas separation systems of membranes with unchanged characteristics, the possibility of full automation of installations, etc. The transport of gases and vapors through non-porous polymer membranes is traditionally described by the "dissolution-diffusion" model [13]. In this model, the process is represented as consisting of the following stages: sorption and dissolution of the gas in the polymer matrix on one side of the membrane, diffusion of the dissolved gas through the polymer (membrane) and separation (desorption) of the gas from the polymer on the other side of the membrane. In addition to air separation, membrane technologies can be used in electronics [14].

One of the promising directions for the development of air separation plants and in particular medical separation plants is the combination of adsorption and membrane separation methods in a single device in order to increase the energy efficiency of the oxygen production process [15].

The aim of this work is to study the sorption properties of zeolites NaX [16] and HF 512O (CaNaA [17]), to obtain sorption isotherms and to determine a suitable zeolite for use in a membrane-adsorption oxygen concentrator.

2. Statement of the problem

In the process of studying the sorption properties of zeolites, a volumetric method was used to obtain gas adsorption isotherms [18]. The essence of the volumetric method is to measure the amount of substance in the space above the solid adsorbent. Two containers are required to perform research using the volumetric method. In the first container of a known volume, the pressure of the adsorbed gas or steam is measured, after which the container is connected to a second container filled with a solid adsorbent, the pressure in which is also pre-measured. The container with a solid adsorbent-zeolite can be additionally pre-vacuumed. After combining the tanks in the system, the steady-state equilibrium pressure is measured. Since the air in a certain approximation sufficient for practical calculations is well described by the ideal gas model, then at the working volumes and temperature of the gas phase known for both tanks, using the Clapeyron-Mendeleev equation, it is possible to calculate the number of moles of gas before and after adsorption, and by their difference determine the amount of the adsorbed substance.

To determine the amount of the adsorbed substance, first of all, it is necessary to determine the volume of the adsorber that is not occupied by a solid adsorbent. In the study, synthetic zeolites in the form of balls were used as adsorbents, but the zeolite has a developed surface and internal areas that are accessible to gases, so it is not enough to know the volume of zeolite granules (balls) to determine the free volume of the adsorbent filled with zeolite. To determine the free volume, we used a gas that practically does not Sorb on these types of zeolites – helium.

To determine the free volume, write down the equations of state of the gas in the tanks before and after combining. In a container filled with gas on the receiver, before combining:

\[ V_0P_0 = \nu_0RT, \]

where \( V_0 \) is the volume of gas in the receiver before joining, \( P_0 \) is the gas pressure in the receiver before joining, \( \nu_0 \) is the amount of substance in the receiver, \( R \) is the universal gas constant, and \( T \) is the gas temperature.

In the second pre pumped to pressure \( P_1 \), container filled with zeolite in the adsorber:

\[ V_{fv}P_1 + V_{com}P_1 = \nu_1RT, \]

where \( V_{fv} \) is the volume available for gas in the adsorbent, \( V_{com} \) is the volume of gas communications, and \( \nu_1 \) is the amount of substance in the adsorbent and communications in the gas phase.
After combining the receiver and the adsorber, the pressure in them will take the value $P_2$, and the equation of state of the ideal gas will take the following form:

$$V_0 P_2 + V_{fv} P_2 + V_{com} P_2 = v_2 RT,$$

(3)

where $v_2$ is the total amount of substance in the receiver-communication-adsorber system.

Since weakly absorbing helium is used to determine the free volume, then the amount of matter in the gas phase of the system before and after combining practically does not change and can be written as follows:

$$v_2 = v_0 + v_1$$

(4)

Having solved the system of equations 1-4, we get the equation for determining the free volume of the adsorber:

$$V_{fv} = V_0 (\frac{P_0 - P_2}{P_2 - P_1}) - V_{com}$$

(5)

In the case of adsorbed gas, the equations of state of the ideal gas after combining (3) and equation (4) will take the form:

$$V_0 P_2 + V_{fv} P_2 + V_{com} P_2 = v_2 RT + v_{ads} RT,$$

$$v_{ads} = v_0 + v_1 - v_2,$$

(6)

(7)

where $v_{ads}$ is the amount of gas adsorbed on the zeolite.

Device description.

Installation for determining the sorption properties of zeolites is shown in figure 1. The installation consists of two tanks. The first container (1) of a known volume serves as a receiver; the second container (2) is filled with solid zeolite, the sorption properties of which must be checked. Each of the tanks has one inlet and two outlet pipes. The adsorbed gas (helium, nitrogen, oxygen, air) from the cylinder 3 enters the unit through the inlet pipe of the receiver and the crane 6 and reducer 4 installed on it. The output pipes of the receiver are combined and connected via a tap 7 to the manovacuummeter 5, to control the excess gas pressure in the receiver. The inlet pipe of the adsorber 2 through the tap 8 is also connected to the manovacuummeter 5, which allows determining the pressure in the adsorber 2 when the tap 7 is closed. One of the outlet pipes of the adsorber is connected via a tap 9 to a vacuum pump 11 installed in the system for the regeneration of zeolite by vacuum, and the second through a tap 10 allows you to dump the excess pressure of the adsorber 2 into the atmosphere and carry out the regeneration of zeolite at atmospheric pressure.

![Figure 1](image_url)

**Figure 1.** Schematic diagram of the installation for determining the sorption properties of zeolites: 1-receiver; 2 – adsorber; 3 – gas balloon; 4 – gas reducer; 5 – manovacuummeter; 6-10 – valve; 11- vacuum pump.

Gas enters the system from gas cylinders to the receiver. The gas pressure in the receiver rises to a certain pressure controlled by a manovacuummeter. When the required pressure is reached in the receiver, the manovacuummeter is cut off from the receiver and connected to the adsorber, where the vacuum regeneration of the adsorbent is performed using a pump. After regeneration, the adsorber is cut off from the pump by a tap and connected to the receiver filled with gas; the steady pressure is determined by the manovacuummeter. After the experiment, the non-sorbed gas can be released into the atmosphere for atmospheric pressure regeneration.
3. Results and discussion
Determining the free volume. Using the volumetric method of investigation, the experimental data necessary for determining the free volume of the adsorbent were obtained: the pressure in the receiver before combining, the pressure in the adsorbent before combining, and the pressure in the adsorbent after combining. The free volume of the adsorbers was calculated using the formula (5). As a result of experiments and subsequent calculations, the free volume was determined for two adsorbers filled with HF 512O and NaX zeolites, in addition, the volume of the empty adsorber was determined. The average values of free volumes are calculated based on experimental data:

- For an empty adsorber: $V_{fv} = (684 \pm 10)$ ml;
- For adsorber with HF 512O: $V_{fv} = (505 \pm 11)$ ml;
- For adsorber with NaX: $V_{fv} = (492 \pm 10)$ ml;

In addition, the mass of zeolite contained in each adsorber was determined. The true and bulk density of zeolites, the porosity of the adsorbent and the free volume are calculated, taking into account the volume of the empty adsorbent determined by the volumetric method. The calculation results are shown in table 1. It can be seen that the values of free volumes of adsorbers determined on a straight line by the volumetric method and calculated through porosity, taking into account the error, coincide.

| Table 1. The calculation results |
|---------------------------------|
|      | m g | $\rho_{td}$ g/ml | $\rho_{bd}$ g/ml | $\Pi$ % | $V_{fv}$ ml |
| HF 512O | 388.9 | 2.37 | 0.58 | 75.47 | 509.4 |
| NaX | 400.6 | 2.26 | 0.60 | 73.50 | 496.2 |

Figure 2 shows the dependence of the free volume of the adsorbers on the pressure in the adsorber after combining.

![Figure 2](image.png)

**Figure 2.** The dependence of the free volume of the adsorber on the pressure in the adsorber: 1- empty, 2- with HF512O zeolite, 3- with NaX zeolite.
The weak change in the sorption volume from the pressure during the experiment is linear, which corresponds to the absence or very weak adsorption of helium on zeolites. The main contribution to the error is made by insignificant sorption of helium, instrument and random errors.

Determination of sorption capacities of nitrogen, oxygen and air. To determine the sorption capacities of gases using the volumetric method, the pressure in the tanks before and after their combination was experimentally obtained. In the course of the study, receivers of two known volumes V and 2V were used to expand the range of the measured isotherm. For each of them, pressure measurements were made in the receiver (P₀) and the adsorber (P₁) before combining and the adsorber after combining (P₂) for nitrogen, oxygen and air. The step of changing the pressure in the receiver to expansion for V and 2V is 0.25 and 0.5 atm, respectively.

Obtaining sorption isotherms. For modeling and calculations, so-called sorption isotherms are most often used. To obtain sorption isotherms from experimental data, it is necessary to determine the amount of adsorbed gas per gram of substance. To do this, you need to calculate the molar volume for each pressure value and know the mass of the degassed adsorbent. The mass of sorbents is indicated in table 1, and the molar volume is determined according to Avogadro's law:

\[ V_m = \frac{RT}{P}, \]

where T is the absolute temperature and R is the universal gas constant.

The obtained adsorption isotherms for HF 512O and NaX zeolites are shown in figure 3a and 3b, respectively.

![Figure 3. Nitrogen, oxygen and air sorption isotherms on HF 512O (a) and NaX (b) zeolite](image-url)

It can be seen that the sorption isotherms, in contrast to the sorbed volumes, are linear in nature. Thus, the isotherms can be described by the Henry equation:

\[ \nu = k \times P, \]

where k – Henry’s constant.

Selectivity for pure gases. Figure 5 shows that the sorption value of zeolite HF 512O on nitrogen is more than 2.5 times greater than the sorption value on NaX, oxygen Sorption on HF512O is 1.5 times higher than the sorption on NaX, which results in air sorption on HF512O 2 times higher than on NaX. The selectivity for the nitrogen-oxygen pair for both zeolites is similar (figure 4). With increasing pressure, the selectivity decreases. In the pressure range from 1 to 2 atmospheres, the selectivity of HF 512O varies from 2.6 to 2.4, and the selectivity of NaX in the range from 2 to 1.8.

Thus, the most suitable sorbent for use in a membrane -adsorption oxygen concentrator due to its high selectivity and nitrogen sorption capacity is HF 512O. The Sorption capacity of this zeolite is 2.5 times higher than the sorption capacity of NaX zeolite, and the selectivity is 30% higher. The experimental data obtained as a result of the study will be used to refine the mathematical description of selective mass transfer in hybrid membrane-adsorption systems [19].
4. Conclusions
The sorption properties of NaX and HF 512O zeolites were studied at a pressure range from 0.5 to 2 atmospheres. Sorption isotherms and sorption capacities of nitrogen and oxygen were obtained. The selectivity of zeolites for the nitrogen-oxygen pair was determined: 2–1.8 for NeX and 2.6–2.4 for HF 512O. As a result of experiments, it was revealed that the most promising zeolite for use in a membrane-adsorption oxygen concentrator is HF 512O zeolite.

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