

## Composite Sorption-Active Materials Based on Zeolite and Ethylene Fluorine Derivatives

### Part II. Preparation of Composite Sorption-Active Materials, Investigation of Their Physicochemical Properties and Selection of Optimal Synthesis Conditions

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#### Abstract

Experimental studies of methods for obtaining composite sorption-active materials NaX-based crystalline zeolite have been performed. The organic polymers of the fluorine derivatives of ethylene  $[-CF_2-CF_2-]_n$  with a high Young's modulus were used as the binding material. It has been experimentally proved that composite sorption-active materials have unchangeable physical form, a high adsorption capacity and are able to level the strain stresses caused by cyclic loads on the adsorbent in gas separation systems implementing the pressure swing adsorption technology. The choice of the "adsorbent-filler-polymer matrix" composition in the synthesis of sheet, granular and block composite sorption-active materials was scientifically justified. The influence of the types, the ratios of the initial components and the molding conditions on the mechanical and adsorption properties of the composite adsorbent were investigated experimentally. It was found that the dynamic activity on water vapor in synthesized control samples of composite adsorbents was 20–40 % higher compared to traditional industrial adsorbents such as NaX-B-1G.

#### Keywords

Human life support system; adsorbent; composite sorption-active materials; pressure swing adsorption; gas mixture; polymer matrix; zeolite; dynamic activity; tensile strength.

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#### Introduction

As follows from the literature [1–3], when creating adsorbing materials, their shape is important because of the design of the product in which the adsorbent material is used. The use of adsorbing materials in gas separation systems makes it possible to use them in various geometric configurations, such as granules, blocks, sheets, etc. For example, adsorbents in the form of sheets with a maximum surface area are used to dehydrate air in descent space vehicles, while devices with granular adsorbents are used for concentration of oxygen from the surrounding medium for pilots.

In [4–7], various methods of creating composite sorption-active materials were proposed, thus making it possible to design adsorbing materials of various geometric configurations – sheet, porous sheet, granular, and block.

In accordance with these techniques, a number of samples of composite sorption-active materials were made under various process conditions: the ratio adsorbent ( $A$ ): binder ( $B$ ); the amount of solvent ( $S$ ) with respect to the binder ( $B$ ); the temperature of the added water (or substrate – for sheet materials)  $T_w$ ; the temperature in vacuum-drying cabinet  $T_{ab}$ ; duration of vacuuming,  $\tau$ . (Table 1).

Table 1

**Process parameters of manufacturing granulated and sheet composite sorption-active materials (CSAMs)**

No.	A:B, % wt.	S, m <sup>3</sup> /kg	T <sub>w</sub> , °C	T <sub>db</sub> , °C	τ, h
1	75 25	0,025	50	140	5
2	78 22	0,015	55	150	
3	80 20	0,030	65		
4	84 16	0,020	75		4
5	85 15	0,024	90	160	
6	86 14		70		
7	87 13	0,022	85		
8	90 10	0,021	80		

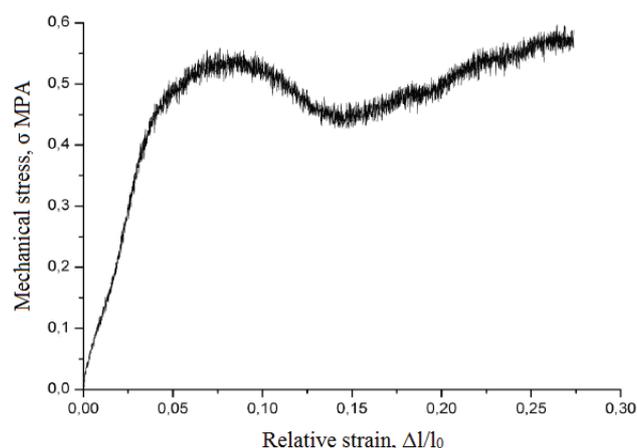
The resulting samples of composite sorption-active materials were further subjected to complex studies.

### 1. Studies of physical-chemical properties of the resulting composite sorption-active materials

#### 1.1. Resistance to mechanical impact

In the study of the resistance to mechanical impact for compression, CSAM samples made at a solvent removal temperature of 60 °C were used, and in stretching experiments, CSAM samples produced at a solvent removal temperature of 45 °C were used. The compression and tensile tests of all the investigated sorption-active materials have shown that the shape of the strain curve remains practically unchanged at floating values of mechanical stress and relative deformation [4–6]. Fig. 1 shows a typical form of the strain curve of the CSAM sample (the ratio of A : B is 85 : 15).

As can be seen from the graph in Fig. 1, the curve has a non-monotonic character. In the section of relative strain variation  $\Delta l/l_0$  from 0 to 0.02, elastic deformation is observed, replaced by the area of plastic deformation ( $\Delta l/l_0$  from 0.02 to 0.09). At  $\Delta l/l_0 \sim 0.09$ , irreversible destruction of the sample is observed, as evidenced by a subsequent decrease in the modulus of the force applied to the sample. Further wave-like behavior of the curve  $\sigma(\Delta l/l_0)$  indicates a sequence of subsequent destructive processes occurring in the volume of the sample under load. This type of deformation is characteristic of materials that are highly heterogeneous in structure, in particular, porous materials with an irregular macroporous structure.



**Fig. 1 Graph of the dependence of the CSAM sample's force response on its relative strain**

Table 2

#### Mechanical properties of the CSAM samples

A:B, % wt.	75:25	80:20	83:17	85:15	87:13	90:10
σ, MPa	0.49	0.51	0.52	0.54	0.58	0.65
E, MPa	13.00	12.40	12.20	12.00	11.70	9.40

The experimental values of the tensile strength  $\sigma$  and the Young modulus E for different ratios A : B at a solvent removal temperature of 60 °C are shown in Table 2.

As it follows from the analysis of the data in Table 2, the maximum strength  $\sigma = 0.65$  MPa is reached at a ratio of zeolite and binder 90 : 10, and the maximum elasticity  $E = 13$  MPa is reached at a ratio of 75 : 25. The best combination of strength and elastic properties of the resulting CSAM is achieved at a ratio of 83 : 17.

It follows from the presented data that the mechanical properties of composite sorption-active materials determined by the value of the Young's modulus increase with the content of the polymer matrix, while resistance to mechanical impact for compression decreases. The latter fact can be explained by an increase in the volume of secondary pores of CSAM with an increase in the binder content [8, 9].

#### 1.2. Thermal stability

In the world technology of sorbents over the past 10 years, there has been a clear trend of developing new adsorbent materials based on organic polymers

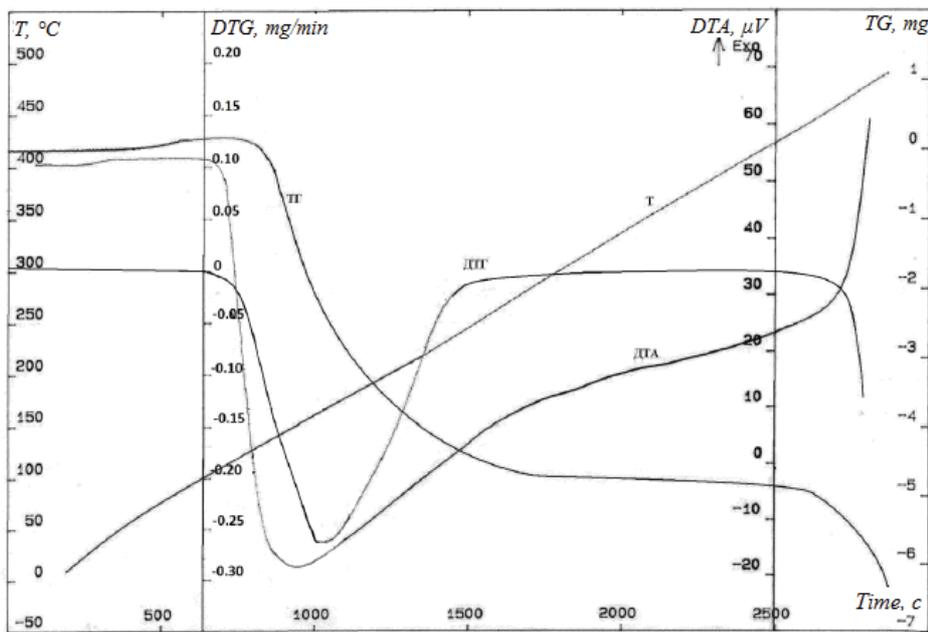


Fig. 2 Results of the thermal analysis of the CSAM sample

capable of leveling deformation stresses caused by a temperature drop, as well as aerodynamic loads on the adsorbent granules. This significantly affects the reduction of dust formation during the operation of the adsorbent (the rate of mass transfer of the adsorbate remains unchanged for numerous adsorption-desorption cycles). In this case, zeolites of various grades, silica gels, alumina, etc. are used as an adsorbent filler, while polyamides, polysulfones, polyolefins, polyethylene terephthalate, etc. or their mixtures are used as a polymer matrix.

However, the above listed polymers have a thermal degradation temperature below 250 °C, which makes it very difficult to carry out their full regeneration, especially if different zeolites are used as the initial adsorbent. Complete desorption of water from adsorbents based on zeolites occurs during thermal regeneration at a temperature of not less than 300–350 °C in vacuum at a residual pressure of 1 kPa or with simple thermal regeneration at 400–450 °C [3]. This leads to a decrease in the adsorption capacity of the adsorbent, a

decrease in the rate of absorption of adsorbate and the degree of its removal from the gas phase in multiple sorption-desorption cycles due to the gradual accumulation of a residual amount of adsorbate in the adsorbent. The development of CSAM resistant to thermal exposure allows for a long-term operation of the material at temperatures above 220 °C [10].

To determine the thermal stability, after the water vapor adsorption stage the synthesized samples of composite sorption-active materials were subjected to thermogravimetric analysis (TGA). The studies were performed in air at atmospheric pressure in the temperature range from 20 to 500 °C. During the experiments, it was found that

the nature of the TGA curves and the differential thermal analysis (DTA) of all samples of composite sorption-active materials is similar. For illustration, Fig. 2 shows the results of thermal studies of the CSAM sample No. 5 from Table 1.

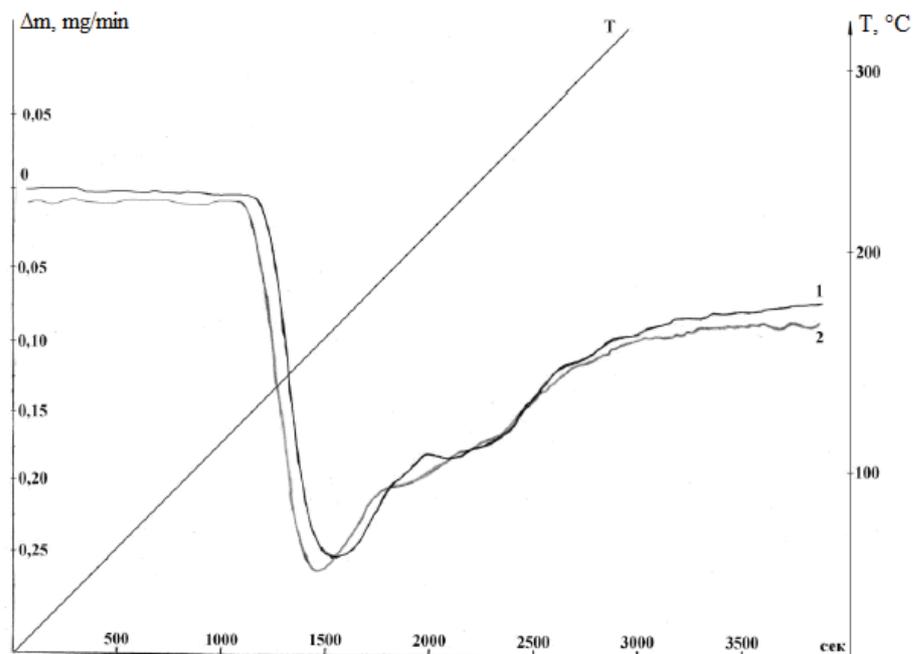


Fig. 3 Thermal analysis of the studied adsorbent materials:  
1 – DTG curve of CSAM sample No 3 from Table 1;  
2 – DTG curve of the initial NaX crystallite

As it follows from the results of thermal analysis, in the temperature range from 80 to 280 °C, a broad band of endothermic effect is observed on the DTA curve, which is accompanied by intensive weight loss (26.1 %). In the indicated temperature range, complete removal of water from the studied samples of composite sorption-active materials takes place. At a temperature of ~430–450 °C (depending on the composition of the sample), the process of destruction of the sample begins, accompanied by a significant exothermic effect on the DTA curve and a decrease in weight.

Under identical conditions, the initial NaX crystallite was studied by the DTA method. It was found (Fig. 3) that the nature and shape of the DTA and DTG curves for the CSAM samples and the pure NaX crystallite samples after the water vapor adsorption stage are absolutely identical in the 25 to 300 °C range (characterizing the desorption process of water). This allows us to conclude that the binder in the form of fluoroplastic (“F-42V” fluoroplastic), added to the adsorbent material does not affect the mechanism and kinetics of the desorption process of water [10].

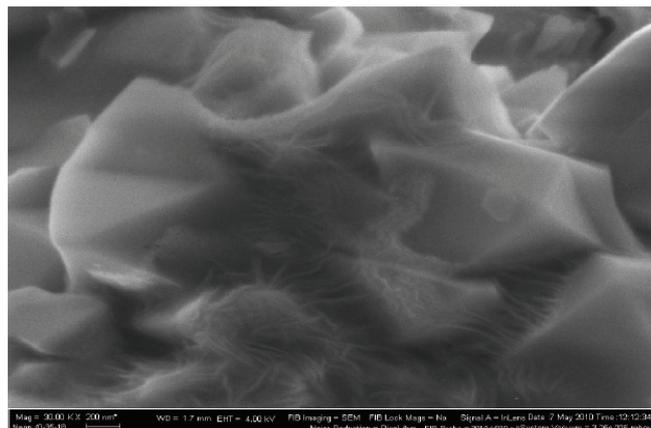
### 1.3. Morphological studies of composite sorption-active materials

The results of a study of the continuity of a film from a polymer matrix of samples of composite sorption-active materials by the scanning electron microscopy method (Neon microscope of CarlZeiss firm) are presented in photographs of segments of the CSAM sample (ratio  $A : B$  is 83 : 17) in Fig. 4.

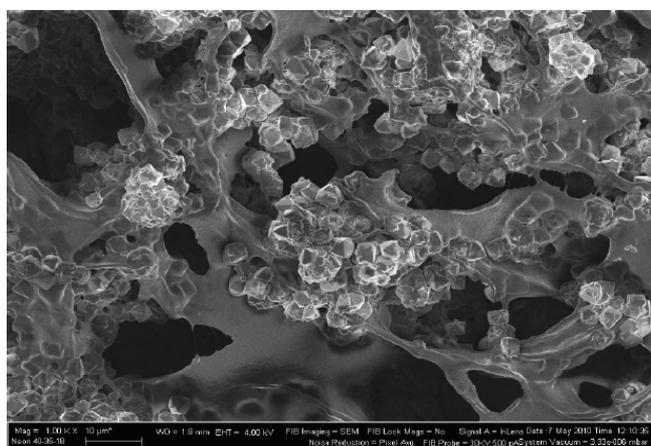
As can be seen from the photographs, in the film of the polymer matrix there are a lot of through transport pores with a diameter of 1 to 10  $\mu\text{m}$ . The adsorbent filler is firmly fixed in the matrix, without blocking its pores (the macromolecules of the binder are an order of magnitude larger than the pore size of the adsorbent), thereby allowing gas to have access to the entire volume of the adsorbent material and without causing significant diffusion resistance.

## 2. Selecting the main process parameters for the manufacture of composite sorption-active materials

The studies found a correlation between the main operational properties of the resulting CSAMs (static and dynamic capacity, kinetics of adsorbate mass transfer in adsorption-desorption cycles, resistance to mechanical action, long-term operational temperature, etc.) and process parameters of cyclic adsorption-desorption processes.



a)



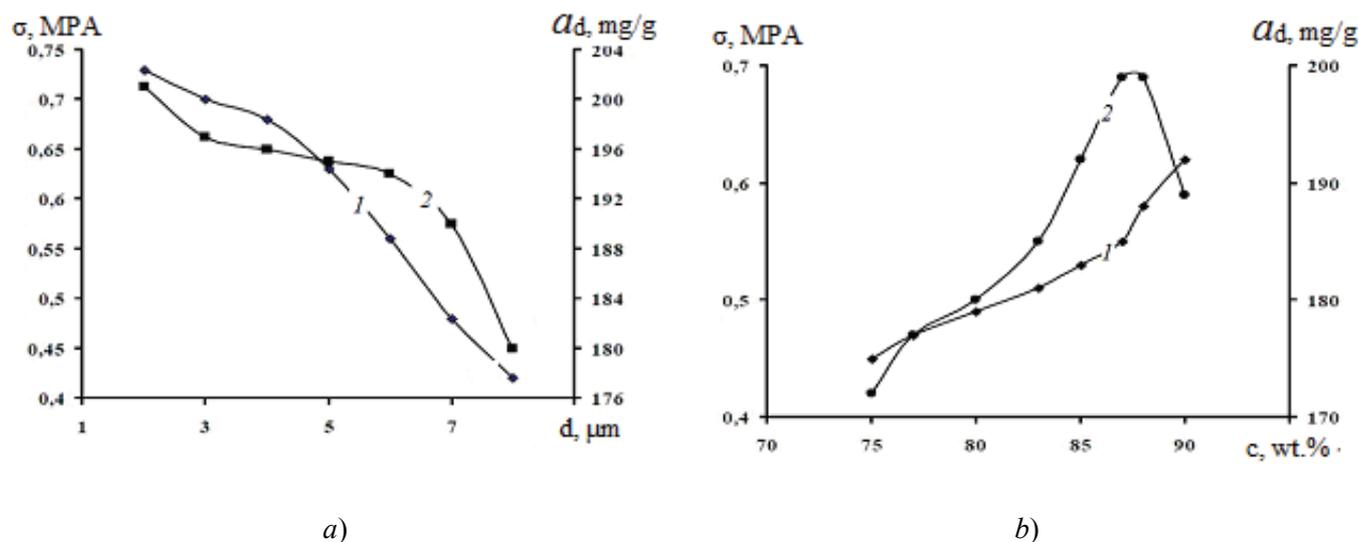
b)

**Fig. 4. Micrographs of CSAM samples:**  
a – magnification by 3000 times;  
b – magnification by 1000 times

### 2.1. Determining the composition and dispersity of initial adsorbent fillers

The studies showed that the use of fine particles as an adsorbent filler leads to a reduction in the defectiveness of the final product and its hardening due to mechanical-chemical activation; causes the formation of a developed secondary porous structure (and, accordingly, improves the kinetics of mass transfer of adsorbate in adsorption-desorption cycles). In addition, the size of the adsorbent-filler particles is a significant factor determining the intensity and duration of mixing of the feed mixture prior to the step of forming the composite sorption-active materials.

The results of the study of the impact of the amount of the adsorbent-filler introduced ( $c$ , % wt.) and its dispersion ( $d$ ,  $\mu\text{m}$ ) on the ultimate strength and dynamic capacity of the resulting block CCAM are shown in Fig. 5.



**Fig. 5. Impact of:**

*a* – dispersity  $d$  of the initial adsorbent filler (crystallite NaX);

*b* – its content  $c$  in the CSAM sample on the tensile strength  $\sigma$  (1) and the dynamic capacity  $a_d$  (2)

From the analysis of the experimental dependences presented in Fig. 5a it is evident that as the size of the particles of the initial adsorbent filler increases, the values of the tensile strength and dynamic capacity decrease. This is explained by the fact that as the dispersion of the adsorbent filler increases, the specific surface area of the adsorbent decreases, which reduces the mass transfer efficiency and increases the diffusion resistance of adsorbate transfer from the gas to the solid phase and vice versa (especially at  $d \geq 6 \mu\text{m}$ ). The decrease in the tensile strength is explained by the decrease in the number of point contacts per unit volume between the adsorbent filler particles and the matrix [11].

Increase in the dispersity of the initial zeolite powder above  $6 \mu\text{m}$  led to a deterioration in the performance characteristics of the adsorbent material. In multiple adsorption-desorption cycles, the precipitation of zeolite particles from the polymer matrix was observed, leading to a decrease in the adsorbent capacity due to the blocking of the transport pores of the adsorbent filler with the fine particle fraction and the growth of the aerodynamic resistance to gas flow.

From the analysis of the experimental dependences in Fig. 5b it follows that when the amount of adsorbent in the CSAM increases, its strength and dynamic capacity increase. It can be assumed that an increase in dynamic capacity is associated with a decrease in the thickness of the film of the polymer matrix distributed on the surface of the adsorbent filler and the corresponding decrease in the diffusion resistance to the transfer of the adsorbate.

With an increase in the content of the adsorbent  $\geq 85 \text{ wt.}$ , a sharp decrease in the dynamic capacity of the resulting CSAM was observed. This is explained by the compaction of their structure, the decrease in the volume of transport pores and, as a consequence, the difficult mass transfer of adsorbate into the volume of the adsorbent material. In the production of CSAMs, the best results were achieved with the adsorbent: polymer matrix ratios in the range (80–88) : (20–12), % wt.

### 2.2. Selecting the solvent and the rationale for its consumption per unit of final product

An important factor influencing the quality of the resulting CSAM is the content of the solvent in the initial suspension, which determines the stability in the homogeneous state (which is necessary for the production of homogeneous CSAM and their defectiveness reduction) and the way of molding CSAM. In addition, the amount of solvent and the size of its molecules have a significant effect on the formation of the secondary porous structure of CSAM (which largely determines the dynamic capacity of the adsorbent) during its removal in the drying stage, and affects the bond strength of the adsorbent with the binder.

The results of experimental studies of block CSAMs if  $d = 4\text{--}6 \mu\text{m}$ , solvent removal temperature  $T_S = 50 \text{ }^\circ\text{C}$  and  $T_S = 80 \text{ }^\circ\text{C}$  (dimethyl ketone (2-propanone, acetone) and methyl ethyl ketone (2-butanone) as solvent) and various solvent ratios ( $S$ ): polymer matrix ( $M$ ) are shown in Table 3.

Table 3

**Impact of the ratio of solvents on mechanical  
and adsorption properties of CSAMs**

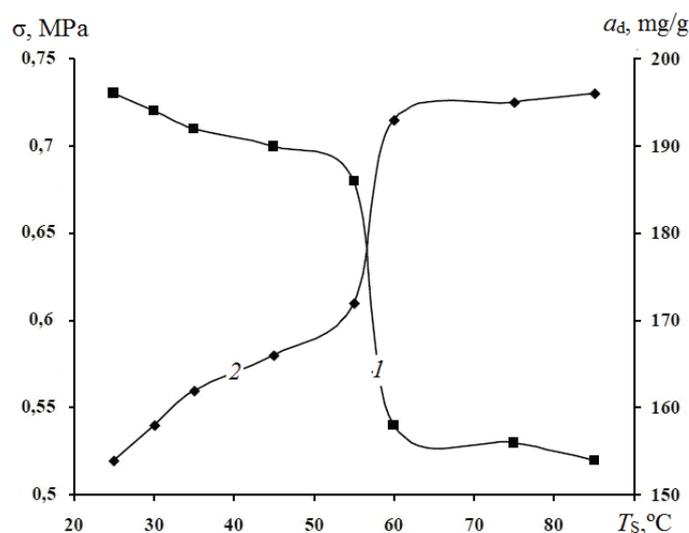
No.	$S : M$ , g/kg : g/kg	Dimethyl ketone		Methyl ethyl ketone		$T_S$ , °C
		$\sigma$ , MPa	$a_d$ , g/kg	$\sigma$ , MPa	$a_d$ , g/kg	
1	10 : 1	0.73	187	0.75	186	
2	15 : 1	0.70	189	0.73	187	
3	20 : 1	0.68	190	0.70	189	
4	25 : 1	0.63	193	0.64	193	50
5	30 : 1	0.56	195	0.59	193	
6	35 : 1	0.48	196	0.54	195	
7	40 : 1	0.42	197	0.47	199	
8	30 : 1	0.52	199	0.51	201	80

From the analysis of data presented in Table 3, it follows that the replacement of acetone with methyl ethyl ketone as a solvent has practically no effect on  $a_d$  and  $\sigma$ . The optimum ratio was  $S : M$  in the range of 15–30 g/kg. If  $S : M \leq 15$  g/kg, the values of dynamic capacity and strength decreased, and the process of molding of CSAM became more complicated due to the high viscosity of the resulting suspension. This is explained by a decrease in the number of transport pores formed when the solvent was removed due to the heterogeneity of the structure of the resulting CSAM.

*2.3. Determining the temperature of molding  
and drying of samples of composite  
sorption-active materials*

The relationship between the solvent removal temperature  $T_S$  in the stage of suspension drying, the dynamic capacity  $a_d$  and the mechanical strength  $\sigma$  is shown in Fig. 6. The solvent used in the creation of CSAM acted as a plasticizer and a blowing agent.

The presented results indicate that an increase in  $T_S$  from 25 to 57 °C led to an increase in the dynamic capacity of the samples studied, while  $\sigma$  decreased. If  $T_S = 55$ –57 °C, a discontinuous change in the properties of CSAM due to the boiling of acetone was observed, accompanied by its intensive release from the formable suspension. At the same time, there was a sharp increase in the number of transport pores (an increase in the volume of the finished CSAM by 2.5–3 times compared with the initial suspension).

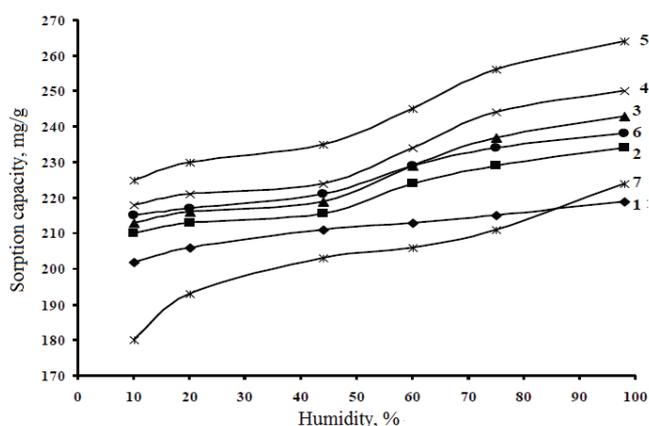


**Fig. 6. Impact of the solvent removal temperature  $T_S$  on the mechanical strength  $\sigma$  (1) and the dynamic capacity of water vapor  $a_d$  of the resulting CSAM (2)**

**3. Investigation of the adsorption  
characteristics of the finished  
composite sorption-active materials**

*3.1. Isotherms of water vapor sorption by samples  
of composite sorption-active materials*

Sorption of water vapor by composite sorption-active materials was investigated both in static and in dynamic conditions under different conditions; these parameters were compared with the same parameters of one of the best commercially available granular



**Fig. 7. Isotherms of the water vapor sorption by adsorbing materials with the ratio  $A : B$ :**  
 1 – 75 : 25; 2 – 80 : 20; 3 – 83 : 17; 4 – 85 : 15; 5 – 87 : 13;  
 6 – 90 : 10; 7 – 90 : 10 – zeolite NaX-B-1G

zeolites NaX-B-1G (TU 6-16-20-90) registered under similar conditions.

Determination of the water vapor sorption isotherm was carried out according to the procedure described in part I of the paper [12]. Fig. 7 shows the results of finding the sorption capacity in relation to water vapor under static conditions by the finished composite sorption-active materials at different air humidity and at a temperature of 25 °C for 5 hours.

The analysis of the isotherms shown in Fig. 7 allows us to conclude that when the content of zeolite in the initial solution exceeds 90 %, the sorption capacity of the finished articles decreases, which is explained by the partial destruction of the adsorbent due to the insufficient amount of binder to provide the required strength. The best zeolite-binder ratio is 87 : 13, which ensures a sorption capacity of up to 265 g/kg.

### 3.2 Kinetics of water vapor sorption by samples of composite sorption-active materials under static conditions

To study the kinetics of the water vapor sorption processes under static conditions, samples of composite sorption-active materials of the same geometric configuration were placed in a desiccator with a fixed content of water vapor in the desiccator atmosphere and recorded a change in the mass of the sample at regular intervals. All experiments conducted at a temperature of  $(20 \pm 2)$  °C. The kinetics of mass transfer of water vapor was investigated for  $n = 20$  sorption-desorption cycles by calculating the amount of water absorbed in time  $t$  at a fixed moisture content  $\phi$ . Desorption of all samples was carried out under the

same conditions – vacuuming at a residual pressure of 1 kPa and a temperature of 100–110 °C for 2 hours, then at a temperature of 140–160 °C for 2-hours (Table 4).

The analysis of the experimental data made it possible to find that the decrease in the adsorption capacity of the CSAM sample ( $A : B = 90 : 10$ ) and NaX-B-1G zeolite after 20 sorption-desorption cycles is explained by the partial destruction of the adsorbent material under the impact of aerodynamic loads, causing the formation of a finely dispersed fraction (dust) and blocking due to the porous structure of the material.

The analysis of the totality of the results on the study of the sorption characteristics of samples of composite sorption-active materials allows us to state that the film of a polymer matrix made of fluoroplastic on the surface of the adsorbent-filler granules does not have continuity, which allows free access of adsorbate molecules to the CSAM volume. The permeability of the polymer matrix film ensures the preservation of the capacitive characteristics of the finished composite sorption-active materials at the level of the initial adsorbent-filler. This conclusion was verified by the results of morphological studies of the finished CSAM using scanning electron microscopy.

The kinetics of water vapor absorption by the CSAMs NaX-based crystallite impregnated into the fluoroplastic matrix is on the average 15–20 % higher than in the granulated zeolite NaX-B-1G, both under static and dynamic conditions. The coefficient of utilization of the equilibrium dynamic capacity [13, 14] for the resulting composite sorption-active materials was in the range of 90–93 %, which indicates a high rate of absorption of water vapor under dynamic conditions.

The resulting absorbent materials provide a longer protective action time and deeper air drying (down to minus 72.4 °C at the dew point) compared to conventional granular NaX adsorbents. The kinetic characteristics of the water vapor absorption of the resulting CSAMs (except for the sample with the ratio  $A : B = 90 : 10$ ) remained unchanged for 20 sorption-desorption cycles, in contrast to NaX-B-1G zeolite, for which a tendency to decrease these parameters was observed. This indicates the constancy of the structure of composite sorption-active materials and the absence of the effect of dust formation during operation [15].

The presented results show that the CSAM samples produced by the proposed technology, using NaX-based crystallite and fluoroplastic matrix have high strength values to mechanical and hydraulic loads and adsorption capacity. The increase in the moisture

Table 4

**Results of the study of the kinetics of water vapor sorption  
by composite sorption-active materials under static conditions**

A:B, % wt.	<i>a</i> , g/kg								
	$\varphi = 10\%$			$\varphi = 44\%$			$\varphi = 75\%$		
	<i>t</i> , min								
	30	60	120	30	60	120	30	60	120
	<i>n</i> = 1								
75/25	162.7	180.8	202.1	176.7	185.4	210.9	195.3	205.2	215.7
80/20	164.1	190.3	211.2	179.8	190.0	215.5	198.2	209.1	228.7
83/17	165.0	194.1	214.3	184.5	197.3	219.6	201.8	214.4	236.9
85/15	168.4	198.7	218.1	189.0	209.5	223.8	212.4	219.7	243.8
S7/13	170.9	204.5	225.6	197.8	221.4	235.8	218.9	225.1	255.9
90/10	170.6	200.0	215.2	197.4	211.0	220.3	211.7	218.8	233.6
NaX-B-IG	141.0	160.3	180.8	151.6	182.1	197.2	182.4	192.7	200.5
	<i>n</i> = 20								
75/25	162.3	180.4	202.0	176.8	185.3	211.0	195.2	205.0	215.5
80/20	164.0	189.6	211.2	179.4	190.1	215.2	197.4	208.7	228.4
83/17	164.7	193.6	214.2	184.6	197.0	219.3	201.4	214.5	236.4
85/15	168.1	198.4	217.8	188.9	209.4	223.6	212.4	219.3	243.3
S7/13	170.7	204.3	225.3	197.6	221.5	235.6	218.4	224.7	255.6
90/10	160.8	192.7	205.6	187.0	201.3	208.9	201.3	209.3	221.2
NaX-B-IG	131.6	151.8	171.4	142.4	171.7	186.6	171.9	177.0	179.3

content at the end of the step did not occur gradually, as it was observed in the case of the use of other solid adsorbent fillers [3, 16, 17], but rather sharply and rapidly, as a result of which it was possible to almost completely use the adsorption capacity of the layer. The dynamic activity of even relatively small layer thickness (~ 0.1 m) of CSAM samples was close to the equilibrium static activity. The results allowed us to conclude about the prospects of using the resulting CSAMs in the systems of drying and separation of gases working on the principle of pressure swing adsorption.

*3.3 Kinetics of water vapor sorption by samples  
of composite sorption-active materials  
under dynamic conditions*

Studies of the sorption characteristics of the CSAM samples under dynamic conditions were performed according to the previously described procedure [3, 18] under the following conditions: the relative humidity of the steam-air flow  $\varphi = 40\%$  (0.007–0.008 kg/m<sup>3</sup>), the temperature of the steam-air

flow ( $20 \pm 2$ ) °C; volumetric specific flow rate  $Q_s = 0.2$  m<sup>3</sup>/(s·m<sup>2</sup>), the height of the layer of the investigated CSAM was 0.150 m.

The results of the experiment are presented in Table 4.

Table 4

**Sorption characteristics of CSAM in dynamic  
conditions with direct air supply**

A : B, % wt.	$\rho$ , kg/m <sup>3</sup>	$T_d$ , °C	$\tau_{pr}$ , min	$a_d$ , g/kg	$k$
75/25	700	-65.3	35	172	0.90
80/20	700	-67.3	36	180	0.92
83/17	710	-72.1	42	187	0.92
85/15	700	-72.3	45	193	0.92
87/13	720	-72.3	46	199	0.93
90/10	740	-70.1	40	196	0.92
NaX-B-1G	1000	-63.2	31	141	0.83

In Table 4  $\rho$  is adsorbent density,  $\text{kg/m}^3$ . The coefficient of utilization of the equilibrium dynamic capacity  $k$  was determined according to [3, 19]. The maximum time of the protective action of  $\tau_{pr}$  and the degree of air dehumidification at the dew point  $T_d$  were reached at a ratio  $A : B$  equal to 87 : 13, which corresponded to the maximum dynamic capacity of the adsorbent (sample No. 5, Fig. 7).

3.4. Study of the porous structure of composite sorption-active materials

The studies were carried out by the bulk method of adsorption-desorption of nitrogen vapors [3]. Samples of sheet composite sorption-active materials produced by the method (Table 5, sample No. 1–4) were used [12]. A sample of NaX crystallite (Table 5, sample No. 5) and a sample of an industrial granular zeolite adsorbent NaX-B-1G manufactured by JSC Rosmkhimzashchita Corporation under TU 6-19-20-90 (Table 5, sample No. 6) were also investigated. In all cases, acetone was used as a solvent in the preparation of CSAM.

The adsorption properties for the samples calculated from the Dubinin-Radushkevich model equation with the affinity coefficient  $\beta = 0.3918$  [3, 20] are presented in Table 6.

Table 5

Comparative characteristics of the porous structure of CSAM samples

No.	$A : M,$ % wt.	$T_s,$ °C	$S : M,$ g/kg : g/kg	$d,$ $\mu\text{m}$	$\rho,$ $\text{kg/m}^3$
1	90 : 10				2050
2	85 : 15				2020
3	80 : 20	50	20		2030
4	75 : 25			4	2010
5	100 : 0				1920
6	87 : 13		–		2150

Table 6

Adsorption properties of CSAM samples

No.	$W_0, \text{cm}^3/\text{g}$	$S_{sp}, \text{m}^2/\text{g}$	$E_0, \text{kJ/mol}$	$d_w, \text{A}$	$D_{meso}, \text{nm}$	$c, \text{\% wt.}$
1	0.308	844.291	16.750	8.950	4.333	89.687
2	0.267	809.460	16.180	9.256	3.504	85.796
3	0.258	736.486	16.670	9.388	2.787	81.178
4	0.244	707.752	16.950	9.306	3.143	75.317
5	0.316	854.876	16.080	9.102	3.114	100.000
6	0.243	733.846	16.110	7.938	1.911	86.986

In Table 6,  $W_0$  is limiting adsorption volume,  $\text{cm}^3/\text{g}$ ,  $S_{sp}$  is specific surface area of CSAM,  $\text{m}^2/\text{g}$ ;  $E_0$  is characteristic energy of adsorption,  $\text{kJ/mol}$ ,  $d_w$  is diameter of the zeolite inlet window,  $\text{A}$ ;  $D_{meso}$  is mesopore diameter,  $\text{nm}$ .

From the analysis of the data presented in Table 6, it can be concluded that the maximum limiting adsorption volume ( $0.308 \text{ cm}^3/\text{g}$ ) was observed when the zeolite content is 89.687 % by weight in CSAM sample No. 1. At higher strength properties, namely, the absence of dust emission during operation, the resulting CSAM sample was comparable with the granular NaX zeolite adsorbent by the value  $W_0$  and by 27 % exceeded it in NaX-B-1G zeolite.

It should be noted that for the samples of composite sorption-active materials, there is a tendency to increase the volume of mesopores and their area with an increase in the content of the adsorbent filler in the CSAM from 75 to 85 %, after which these parameters decrease.

Conclusions

The experimental studies revealed the prospects of using CSAMs in the PSA processes for purification and separation of gas mixtures. The choice of the adsorbent-filler composition was substantiated and verified by the experimental method: the polymer

matrix in the synthesis of CSAM for short-cycle free-gas adsorption plants. It was expedient to use crystalline zeolites with a dispersion of 3–6 μm as initial adsorbent fillers, fluorine derivatives of ethylene (fluoroplasts) as a polymer matrix, and dimethyl ketone (acetone) as the rheological additive. Optimum process parameters for the production of CSAM from NaX-based crystallite and F-42V fluoroplastic were determined: the weight ratio of adsorbent-filler:polymer matrix must be 83 : 17 % by weight, the solvent: polymer matrix ratio must be 15–30 g/kg, the removal of the solvent must be carried out at a temperature of 55–57 °C. This ensures that the maximum adsorption volume of the resulting CSAM is 27 % higher than the granular zeolite adsorbent NaX-B-1G, and the absence of dust release in operation.

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