Study of thermophysical characteristics of composite sorption-active materials for life support systems of manned spacecraft and civil aviation

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Abstract. The method of differential thermal analysis (DTA) was used to study the heat resistance of composite sorption-active materials (CSAM) based on a matrix of fluoroplast and NaX crystallites. Decrease in the temperature of thermal destruction of the polymer matrix by about 90°C was found with an increase in the NaX content in KCAM from 2 to 25% by weight. Using the original method, the thermal conductivity was also studied. The analysis of the totality of the obtained results suggests that the studied parameters depend on the ratio of adsorbent-filler/polymer matrix: with an increase in the binder content in the CSAM from 5 to 25 wt. % thermal conductivity decreases from 0.227 to 0.184 W/mk. This pattern is due to the growth of CSAM mesopores filled with air. The hypothesis is confirmed by the analysis of the secondary porous structure of KSAM

1. Introduction
One of the main parameters of adsorbing materials, on which the calculations of the stages of regeneration and cooling are based, is their thermal conductivity. The higher the thermal conductivity of the material, the less time and energy is required to carry out the stage of its thermal desorption and cooling to the temperature of effective operation. The temperature of effective operation is extremely important for the operation of adsorbents in human life support systems of manned aircrafts operating in a cyclic mode. In addition, it is necessary to know the parameters of the thermal stability of materials in the temperature range of operation in order to avoid their thermal decomposition, which may be accompanied by the release of substances dangerous to the human body. The presented work is a continuation of research on the synthesis and study of the properties of composite sorption-active materials (CSAM) based on fluoroplastics and various adsorbents-fillers [1-8] and is aimed at identifying the regularities of the influence of the amount of adsorbent - filler in CSAM on CSAM thermal stability and thermal conductivity. The work is aimed at identifying the regularities of the influence of the amount of adsorbent filler in CSAM on their thermal stability and thermal conductivity

2. Experimental part
For the research, samples CSAM with the different content of the adsorbent – filler were synthesized, where NaX crystallite was used. Fluoroplast of the brand "F - 42V" was used as a polymer matrix. The essence of all methods for obtaining CSAM is the preparation of a suspension of the adsorbent - filler
in a polymer solution, the formation of the resulting suspension and the removal of the solvent by thermal vacuum drying. The molding was carried out by injection or casting methods [1 - 4].

The thermal stability of the obtained CSAM was studied on the TAG – 24 research complex of the «Setaram» company by thermogravimetric and differential thermal analysis under non-isothermal conditions. Samples weighing 20-80 mg were studied after the stage of water vapor sorption. This ensures uniform heating of the sample during the experiment and excludes the presence of effects on the thermograms that correspond to the transition from a non-equilibrium state to an equilibrium state and can affect the correctness of the obtained data [5, 9]. The studies were carried out in a corundum crucible in the temperature range from 20 to 500°C in air at atmospheric pressure. The choice of experimental conditions is due to the fact that it is under these conditions that the thermal regeneration of zeolite-based adsorbents occurs, accompanied by maximum impact on the material [5,6]. Changes in the mass of the samples were recorded with an accuracy of 0.01 mg, the temperature-with an accuracy of 0.10 °C. To measure the temperature, a platinum-platinum-rhodium thermocouple was used, graded according to generally accepted reference points and placed in the volume of the sample under study.

The studies were carried out at a heating rate of 5-10 degrees per minute, which ensures the identity of temperatures throughout the entire volume of the studied samples during the experiment. When the heating rate of the samples is higher than 12 degrees / min and less than 5 degrees/min, a significant deviation of the temperature curve T from a straight line is observed, which can affect the reliability of the obtained results. This experimental fact is explained by the violation of the equality of temperatures of the outer and inner layers of the sample, caused by insufficient thermal conductivity of the materials [5].

When interpreting the experimental data, it was found that the nature of the TGA and DTA curves of all CSAM samples was similar regardless of the method of preparation. In order to avoid cluttering with the same type of graphs, the results of thermal studies of the CSAM sample (the weight ratio of the polymer matrix/adsorbent – filler is 13/87) obtained by dehydrating the adsorbent – filler suspension in a fluoroplast solution in the microwave field are given as an example [4]. However, it was noted that the position on the DTA curve of the peak corresponding to the process of thermal destruction of the polymer matrix depends on the amount of adsorbent filler in the composition of the CSAM, which will be discussed below.

During the experiments, it was found that at a temperature of 91.7±1.5 °C, the process of desorption of water vapor from the CSAM begins, passing through a maximum at 172.7±1.1 °C and ending at 275.8±1.9 °C (the first endothermic effect on the DTA and DTG curves). At the same time, there is a decrease in the mass of the studied CSAM samples by 26.0±0.2%, (the total sorption capacity of the sample is ~ 26.1% by weight), which indicates almost complete desorption of water vapor from the samples of adsorbing materials under experimental conditions. This postulate was confirmed by the results of gas chromatography analysis of gaseous substances released from the CSAM in the temperature range of 75 – 250°C: only water molecules and acetone in a small amount were recorded as a solvent used at the synthesis stage.

The presence of only one endothermic effect in the temperature range from 80°C to 280°C on the DTA curves clearly indicates that in the process of desorption, energy is spent only on one stage - the separation of adsorbate molecules from the surface of the adsorbent. The correctness of this assumption is also confirmed by the fact that the curves of DTH and DTA desorption of water from the NaX and CSAM crystallite are practically identical [1]. This indicates that there is no influence of the fluoroplast matrix and the diffusion of adsorbate in the secondary porous structure of the adsorbing materials on the activation energy of the desorption process. This conclusion confirms the absence of influence on the main kinetic parameters of the desorption process of the dispersion of crystalline zeolite NaX [1].

It follows from the results of thermal analysis that in the temperature range ~ 405 - 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 (up to 45% by weight, depending on the composition of the sample) and having a maximum in the temperature range ~ 455 - 470°C. Moreover, in the above temperature range, this effect is observed in all the studied CSAM samples, regardless of the dispersion of the initial adsorbent - filler and the method of preparation. It is interesting to note the fact that no effects were recorded during the thermal analysis at temperatures
comparable to 360 °C (according to the literature data, the decomposition temperature of the F-42B grade fluoroplast). It is logical to make an assumption about an increase in the thermal stability of the polymer matrix KCAM due to the presence of zeolite NaX (the facts of the influence of inorganic components on the physical transitions of polymers are described in [12]).

![Figure 1. Complex thermal analysis of CSAM based on NaX zeolite and a fluoroplastic matrix.](image1)

![Figure 2. The dependence of the temperature of thermal destruction of the polymer matrix CSAM on the content of the adsorbent filler.](image2)

To confirm the hypothesis that the thermal stability of the fluoroplast matrix was increased due to the presence of zeolite NaX, a thermal analysis of CSAM samples was carried out, the content of the adsorbent filler in which varied from 2 to 50% by weight. The revealed dependence of the change in the temperature of the beginning of thermal destruction of the polymer matrix on the content of the adsorbent filler in the CSAM is illustrated in Figure 2.

It follows from the presented graphic material that with an increase in the content of the adsorbent filler (in this case, zeolite NaX) in the composition of the CSAM from 3 to 26% by weight, the temperature of the beginning of the destruction of the matrix from fluoroplast F-42 increases from 405°C to 449°C. A further increase in the content of the adsorbent filler has an insignificant effect on the temperature of the beginning of the destructive processes.

When determining the thermal conductivity of adsorbing materials, a specially manufactured measuring device was used and an original technique was used that allows measuring this parameter for samples that do not have an almost smooth surface (to which all CSAM belong) [6,7]. Samples of adsorbing materials weighting 1.0 - 1.1 g were used as the object of research.

As is known from the theory of adsorption, significant adjustments to the value of the effective coefficient of thermal conductivity can be made by the thermal conductivity of the experimental medium, the thermal conductivity of the sorbate and the convection of heat by the desorbate released from the solid phase at the regeneration stage [10, 11], etc. Therefore, to level these factors, experiments to determine the thermal conductivity of the studied samples were carried out in a vacuum after the desorption stage.

During the first series of experiments, the studied samples contained 80 % of the weight adsorbent – filler and 20 % of the weight binder-fluoroplast for CSAM and clay for zeolite NaX-B-1G. The thermal conductivity of the materials was studied in the temperature range of 20-160 °C. The results of the experiments are shown in Figure 3. From the presented graphical data, it can be seen that the thermal conductivity of the obtained CSAM is 10-13% higher than that of the serial zeolite NaX-B-1G. The obtained results can be explained by the superposition of two factors: a higher thermal conductivity of the fluoroplast compared to clay and a large number of point contacts between the particles of the adsorbent filler and the matrix in the CSAM.
The following experiments were aimed at identifying the relationship between the thermal conductivity of CSAM and the content of an adsorbent filler in their composition. Materials containing from 75 to 90% of the weight adsorbent - filler with a dispersion of 4-6 microns were studied. To neutralize the possible influence of various factors, all other parameters of obtaining CSAM remained unchanged [2,3]. The thermal conductivity of the CSAM in this series of experiments was recorded at 80 °C. The results obtained are illustrated in Figure 4.

It follows from the above results that with an increase in the content of adsorbent filler in the CSAM from 75 to 90% by weight, their thermal conductivity improves, which, in our opinion, is due to a decrease in the number and volume of transport pores filled with air – a poor conductor of heat. This assumption is indirectly supported by the results obtained earlier by the authors [6 - 8] on the relationship of the kinetics of the sorbate mass transfer processes in the sorption-desorption cycles with the content of an adsorbent filler in the CSAM, which affects the secondary porous structure of the material. To confirm this hypothesis, studies of the secondary porous structure of CSAM samples obtained at different adsorbent – filler/polymer matrix ratios were carried out. The study of the porous structure was carried out on the basis of the study of the adsorption-desorption isotherms of nitrogen vapor in the range of relative pressures from 0.0025 to 0.995 on the NOVA-1200e gas sorption meter manufactured by Quantachrome Ins. (USA). Data registration and processing were carried out using the NovaWin V. 11.0 software with the use of the Dubinin – Radushkevich (DR) model equation [10,11] with a similarity coefficient (affinity) equal to 1 (standard nitrogen vapor). For all the studied samples, nitrogen adsorption isotherms belong to the I structural type in accordance with the IUPAC classification, characteristic of microporous adsorbents, while there are no significant phenomena of adsorption hysteresis. The adsorption properties calculated based on the model equation of DR with a similarity coefficient (affinity) $\beta = 1.0$ and the characteristics of the secondary porous structure of adsorbing materials determined by the BJH method [11] for nitrogen desorption isotherms are presented in Table 1.

| Model # | Adsorbent-filler/polymer matrix ratio, % weight | $E_0$, kJ/mol | $V_{meso}$, cc/gr | $S_{spec}$, m$^2$/gr | $d_{meso}$, nm |
|---------|------------------------------------------------|---------------|------------------|-----------------------|----------------|
| 1       | 90/10                                           | 16.64         | 0.007            | 5.341                 | 2.815         |
| 2       | 85/15                                           | 16.32         | 0.011            | 7.621                 | 2.982         |
| 3       | 80/20                                           | 16.28         | 0.017            | 10.735                | 3.437         |
| 4       | 75/25                                           | 16.12         | 0.022            | 14.587                | 4.314         |
It is interesting to note the fact that for the studied samples of CSAM, there is a tendency to reduce the volume of mesapores and the specific surface area with an increase in the content of the adsorbent-filler in CSAM from 75 to 90%. Thus, the obtained results confirm the hypothesis about the nature of dependence of the secondary porous structure of the obtained materials on the ratio of adsorbent-filler/polymer matrix.

3. Conclusions
1. The analysis of conducted studies of thermal resistance CSAM to corrosion based on zeolite NaX and a matrix of fluoroplast of the brand "F-42B" allows asserting that the thermal destruction of the matrix begins in the temperature range of 405-453°C, depending on the composition of the sample. The fact of increasing the heat resistance of the polymer matrix made of fluoroplast of the brand "F - 42B" by 45 – 900°C with the introduction of more than 3% by weight of NaX zeolite into it was established.
2. It is established that the thermal conductivity of the CSAM depends on the ratio of adsorbent-filler/polymer matrix: with an increase in the binder content in the CSAM from 10 to 25 % by weight, the thermal conductivity decreases from 0.227 to 0.184 W/Mk, which is due to an increase in the volume of transport pores of the studied materials from 0.007 to 0.022 cm3/g.

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