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NEW SORBING MATERIAL FOR CLEANING AIR OF CLOSED SPACES

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ABSTRACT

A new high-efficiency filter material for purification of the air in enclosed spaces is created. Sorbent, as in the form of small and large particles, has a large specific surface, which makes it possible to use it to capture toxicants from water and air, and the sorption characteristics of the latter remain high. The physical-mechanical (abrasion, grindability, "conventional mechanical strength") and the adsorption structure (porosity, sorption activity of iodine, of benzene, lightening capacity for methylene blue, ash content, total porosity) characteristics of the sorbent are studied. The adsorption of hydrogen sulfide, sulfur dioxide and carbon dioxide from the atmosphere is studied. The results were used to calculate the thermodynamic and equilibrium sorption properties of a number of toxicants on sorbent. According to the experimental results of the adsorption of acid gases from the air thermodynamic characteristics, indicating the formation of adsorption complexes of high durability are obtained. Found that 1 gram of sorbent can absorb 640 mg of sulfur dioxide, hydrogen sulfide 300 mg and 350 mg of carbon dioxide that can be recommended sorbent for purification of the air in enclosed spaces.

KEYWORDS: sorbent material, air conditioning, abrasion, grindability, mechanical strength.

INTRODUCTION

He air surrounding us is one of the main components of ensuring life on earth. To maintain the vital processes of living organisms, air that does not contain impurities and is homogeneous in compositionn is necessary. With the development of industry and increasing of transport intensity the purity of the atmosphere began to be constantly threatened [1].

The problem of protecting the air basin is to eliminate harmful emissions into the atmosphere in general or to replace the highly toxic substances contained in these emissions with less toxic (almost non-toxic) components. The fight against atmospheric pollution is carried out in three main directions [2]:

1) creation of new technological processes based on a non-waste principle;
2) improvement of technological processes allowing to eliminate or to reduce emissions of toxic substances into the atmosphere;
3) treatment of industrial gas emissions in order to extract impurities and then use them or neutralize their harmful effects on the environment.

The main of these directions is the processing of gas emissions by various technical methods to meet sanitary requirements for the purity of exhaust gases. The choice of methods for purification and neutralization of industrial emissions in the gaseous state or in the form of an aerosol is determined by the specific features of the gas systems (the composition and concentrations of toxicants, gas and dust content characteristics, the frequency of releases to the atmosphere) and by the requirements for the degree of purification. Sorption, chemical, condensation methods and oxidation methods (thermal and catalytic) are used to neutralize gas emissions,. In a number of cases they are effective enough each by itself or in combination with each other. There is no universal method that makes it possible to neutralize toxic products in a wide range of concentrations for various technological processes. In each specific case, the most suitable method determined by technical and economic calculation (or combination of methods) is used.

It should be noted that the creation of various types of cleaning and filtering devices is often associated with high capital investment and operating costs, which leads to a deterioration of such cost-accounting indicators as the cost of production, profitability and return on assets [3].

Earlier we offered a new highly effective sorbent [4] made of expanded clay, covered with a thin layer of pyrolusite (manganese dioxide) to purify atmospheric air in the fluidized bed apparatus. The conducted studies showed a relatively high degree of purification of atmospheric air, which is much higher than the degree of purification of known analogues. At the same time, the main disadvantage of this sorbent is the low sorption of acid gases, such as hydrogen sulphide, sulfur dioxide and carbon dioxide.

We are offering a new sorbent obtained by mixing of finely ground 100 g of portland cement-500 and 100 g of silica clay from the Astrakhan region with 100 cm3 of a 10% aqueous solution of common salt and the formation of granules of the required sizes (0.5 to 5 cm in diameter). After setting and solidification the mass is placed in running water and kept until the water has a negative reaction to the chloride ion, after drying at 80-85° C, the pellets are placed in a 40% aqueous solution of diethanolamine (DEA) for 1 hour. Then the granules are transferred to sieve, this removes the excess of DEA, the granules are dried in an air current (fan) at 20-40° C. The sorbent is designed to purify atmospheric air from acid gases such as hydrogen sulfide, sulfur dioxide, carbon dioxide. The declared sorbent contains a mixture of silica clay with portland cement-500, containing in terms of oxides (wt. %): CaO, SiO_2, Al_2O_3 and additionally diethanolamine and water.

We studied the physic-chemical characteristics of the sorbent. From the physical and mechanical parameters, the following main ones were determined: bulk density, water resistance, wear vibration, mechanical crushing strength at T=105° and 300° C, conventional mechanical strength, abradability, grindability and granulometric composition. These indicators are interrelated and allow to predict the change in the strength characteristics of adsorbents and sorption-filtering materials in the processes of their long-term operation.

MATERIALS AND METHODS

Abradability and grindability

The abradability and grindability were determined as follows: 300 g of the test material was dried at 60° C, screened on sieves with apertures of 1 and 0.5 mm. The material that passed through a 1.0 mm sieve and remained on a 0.5 mm sieve in an amount of 100 g was placed in a 250 cm3 jar and filled with 150 cm3 of distilled water. The jar was closed with a lid and placed for 24 hours in a shaking machine making 120 shakes per minute, then the jar was transferred to a porcelain evaporation dish, evaporated and dried at 60° C. The contents of the dish were scattered successively on 0.5 and 0.25 mm sieves and weighed. The mass of the material passed through a sieve with holes 0.5 mm in diameter, but remaining on a sieve with holes of 0.25 mm in diameter, shows the grindability of the material and is expressed as a percentage. The mass of dust passing through a sieve with holes of 0.25 mm in diameter shows the abrasion of the material and is also expressed as a percentage. 0.64 g of the material passed through a 0.5 mm sieve and remained on a 0.25 mm sieve.

$$\text{Grindability} = \frac{0{,}64 \cdot 100}{100} = 0{,}64 \quad \text{(allowed up to 4\%)}.$$

The sample passed through a No. 0.25 sieve amounted to 12.0 g. Of this amount, dust, less than 0.15 mm, was 11.6 g. The abrasion was determined without taking into account the dust particles equal to $\frac{(12{,}0-11{,}6)\cdot 100}{100}$ =0,4%. The abradability of the material for this purpose should not exceed 0.5%. For this indicator, the sample presented meets the requirements for materials suitable for industrial use.

The determination of "conditional mechanical strength"

The "conditional mechanical strength" is considered as the total loss of the filtering load under conditions simulating the operation of the production filter during the year.

The conditional mechanical strength is determined as follows: 200 g of filter material passed through a sieve with a hole diameter of 2.0 mm and remaining on a sieve with a hole diameter of 0.5 mm is dried to a constant mass at 60° C.

The sample is placed in a glass column with a diameter of 30 and a height of 300 mm and washed with an intensity of 14-15 dm^3/cm^2 for a time corresponding to the total filtration time of the filter for one year (in this case 61 hours).

The conditional mechanical strength is determined by the formula $S = \frac{(A_1 - A_2 + B)}{A_1} \times 100$, where A_1 is the sample of the dry test material, A_2 is the mass of the dry material after washing, and B is the mass of the fraction less than 0.5 mm. The conditional mechanical strength is $S = \frac{(200-146)}{200} \times 100 = 27$. According to the conditional mechanical strength, the presented sample is suitable for use as a load in fast filters. The main physical and mechanical characteristics of the sorbent are given in Table 1.

Table 1. Basic physical and mechanical characteristics of the sorbent

Particle×10^3, m	Bulk density ×10^3, kg/m3	Water resistance, %		Wear vibration, %	Mechanical crushing strength ×10^{-4}, kg/m^2		Abradability, %	Grindability, %	Conditional mechanical strength, %
		With boiling	Without boiling		T=105°C	T=300°C			
20 - 30	0,95	98,50	98,90	0,95	130,0	150,0	0,50	1,80	25,0

An analysis of the physic-mechanical characteristics showed that the bulk density of the initial samples rises from $0.7052 \cdot 10^3$ to $0.95 \cdot 10^3$ kg/m^3. All studied samples, regardless of the size of the particle, have a small percentage of wear vibration: for initial samples it is about 0.95%. Within the limits of the norm, the parameters for grindability and abradability are 0.95 and 1.80% and 0.45 and 0.5% respectively.

Thus, the tested filter material sorbent in terms of "abradability" and "conventional mechanical strength" is suitable for use as a bed in fast filters for cleaning atmospheric air or water [5].

Method for determination of sorption activity by iodine (IRTS No. 6-16-1003-67)

A sample of the test sorbent ~20 g is placed in a flask and filled with 200 cm^3 of 2N solution of HCl. The mixture is heated to reflux for 10 minutes. Then it is washed from excess of HCl with hot distilled water to a residual Cl-ion concentration of not more than 2.0 mg/l, then it is dried at 105-110° C for one hour.

A sample of 1g (G) (1±0.0002g) is placed in a flask, 100 cm^3 of a 0.1N iodine solution is added, capped and shaken for 30 minutes (or 15 minutes continuously). Select 10cm^3 of the solution from this flask and titrate with 0.1N sodium thiosulfate solution with starch as an indicator.

At the same time, the initial content of iodine is determined by titration with 10cm^3 of the initial solution.

Sorption activity is determined by the formula:

$$F = \frac{(V' - V'') \cdot 0.0127 \cdot 100 \cdot 100}{10 \cdot G}, \qquad (1)$$

where *F* is sorption activity by iodine; *V'* is the volume of $Na_2S_2O_8$ for the initial solution of iodine, cm^3; *V''* is the volume of $Na_2S_2O_3$ for the iodine solution after sorption, cm^3; *G* is the weight of the sample of sorbent, g.

Clarifying ability on methylene blue (GOST 4453-48)

About 0.1g of sample sorbent (g_0) is dried for 3 hours at a temperature of 110±3° C, 10 cm^3 of 0.15% aqueous methylene blue solution is added and agitated for 5 minutes. After the first 10 cm^3 of the solution is discolored, 1cm^3 of the methylene blue solution is continued to add until the blue color of the solution has disappeared within 5 minutes.

The clarifying ability is calculated by the formula:

$$E = 5n, \qquad (2)$$

where *E* is clarifying ability, %; *n* is the amount of cm^3 of methylene blue, decolorized by a sample of the test sorbent in 0.1 g; 5 is a factor of 100/20.

Porosity by acetone (GOST 6217-52)

A sample of the test sorbent ~10g (g_0) is placed in a flask and 100 cm^3 of acetone is poured. In 15 minutes the flask is closed with a paper disc and the acetone residues are poured off. The sorbent with absorbed acetone is weighed (g'_0) and the acetone porosity is determined by the following formula:

$$g_0' - g_0 = m_{propanone} = \rho \cdot V, \qquad (3)$$

where g_0 is the mass of the dry sorbent, g; g'_0 is the mass of the wet sorbent, g; ρ is the density of acetone at the temperature of the experiment, V is the volume of acetone.

Determination of benzene activity (GOST 8703-58)

The test sorbent is dried at 105-110° C and placed in a dynamic tube. The volume of the sorbent in the dynamic tube is *V*. Through the dynamic tube, let the steam-air mixture (benzene, air) pass. The concentration of benzene in the steam-air mixture is 30±3 mg/dm^3.

Passage of the steam-air mixture is terminated when the concentration of benzene in the air above the sorbent is 1-2 mg/m^3. Then the tube with the sorbent is removed and weighed:

$$G_{TP} = g_o' - g_0, \qquad (4)$$

where g_0 is the initial mass of the tube with the sorbent, g_0' is the mass of the tube with the sorbent after absorption of benzene.

Next, the tube is placed in its original place and the reaction mixture is passed to a constant weight.

The concentration of benzene up to and after the layer is:

$$X' = \frac{G_{mp}}{V} \cdot 100 \qquad (5)$$

Give values $\frac{x}{x'} \cdot 100/150$. The speed of the steam-air mixture is 0.5 l/min per 1 cm^3, t=15 °C. Preliminary air is dried and cleaned by the filter system, then it enters the mixer (carburetor) and further it enters the dynamic tubes filled with sorbent. Purified of benzene air goes into traction.

During operation, the content of benzene in the air mixture before and after the absorption tube is controlled [6].

The percentage of water determining method (GOST 1259-67)

1. Sampling:

Samples are selected in accordance with the requirements of the technical documentation standards for specific types products. The sample is cut with using a divider in accordance with GOST 16189-70 or by the quarting method (getting mass of 4-6 g, which is needed for analysis) to determine the percentage of water.

2. Apparatus, reagents:

- Drying cabinet with electric heater SSh-3, SSh-150, SSh-0.05;
- Glasses for weighing in accordance with GOST 25336-82 (types: CB-1919, CH-34112) are numbered, dried and weighed and stored in a desiccator with $CaCl_2$ or silica gel, the mass is checked before taking the sample;
- Mercury thermometer GOST 27544-87, the thermometer mercury tank should be installed in the cabinet and at the level of the glasses with a samples;
- Laboratory analytical scales in accordance with GOST 24101-88 of the 2nd class of accuracy with a maximum weighing limit of 200 g;
- Desiccator according to GOST 25336-82 with granulated $CaCl_2$ or silica gel according to GOST 3956-76. $CaCl_2$ is renewed, the silica gel is calcined at 180-200 ° C.
- Spoons for taking a sample, crucibles.

3. Conducting the test:

3.1. 1 g of sample is taken in a glass, (preliminary dried and weighed with a lid, in grams with an accuracy of 0.0001 characters). A glass with the sample is placed in a heated to 105-110 ° C drying cabinet and dried at this temperature for one hour. Then the glass with the sample is taken from the cabinet, cooled in a desiccator and weighed.

3.2. The duration of each drying is calculated from the moment when the temperature in the cabinet after the glasses setting reaches 105-110 ° C.

4. Processing of the results.

4.1. The water content (x) in% is calculated by the formula:

$$X = (m_1 - \frac{m_2}{m_1} - m) \times 100 \quad , \qquad (6)$$

where m is the mass of the glass with the lid, g; m_1 is the mass of the glass with a lid and the sample before drying, g; m^2 is the mass of the glass with the lid and the sample after drying, g.

4.2. The total value is the arithmetic mean of two parallel determinations, rounded to 0.1%.

Determination of ash content (GOST 1259-67)

A grinded sample of the test sorbent with a mass of ~1g is ashed in a previously weighed cast-iron crucible (m_1) in the muffle, which is heated at a temperature of 800±25° C. After ashing, the crucible with the sorbent (m_3) is weighed again and the ash content of the sorbent is determined by the formula:

$$\frac{m_2 - m_3}{m_2 - m_1} \cdot 100 = w_{H_2O} \quad , \qquad (7)$$

where m_1 is the mass of the cast-iron crucible, g; m_2 is the mass of the crucible with sorbent before ashing g; m_3 is the mass of the crucible with sorbent after ashing, g.

Method of the hydrogen index (pH) determination (GOST 4453-48)

To, 50 cm^3 of water is added to 5 g of grinded test sorbent, the mixture is boiled for 3 mintes with using of reflux condenser and quickly filtered. The pH is determined after cooling the system to room temperature.

Total porosity

A deternined amount of the test sorbent (m_1) is placed in a crucible, distilled water is added and left for 15 minutes. Then surplus water is drained and weighed the sorbent (m_2).

The total porosity (V_Σ) is determined by the formula:

$$V_\Sigma = \frac{m_2 - m_1}{m_1 \cdot p_{H_2O}} = \frac{\Delta m}{m_1 \cdot p_{H_2O}} \quad , \qquad (8)$$

Table 2. Basic adsorption-structural parameters of sorbent

Particle×10^3, m	V of Pores by benzene using×10^{-3}, m^3/kg	Sspecific by toluene ×10^{-3}, m^2/kg	AVERAGE PORES DIAMETER, nm		DENSITY ×10^{-3}, kg/m^3		Porosity, %
			By water	By benzene	Real	Packed	
20 - 30	0,350	300	18,5	14,50	1,98	0,95	85,0

RESULTS AND DISCUSSION

Sorbent test

In order to study the sorption in bottles with a capacity of 5 dm^3, a small vacuum (residual pressure ~ 0.6*10^5 N/m^2) was created with a vacuum pump and gases or vapors of the substance were passed through a special branch pipe. The vapors were generated by heating a sample of a substance (acetone, acetaldehyde, alcohols, phenol) in a gas outlet tube or by chemical reaction of copper with sulfuric or nitric acid (SO_2 or NO_2 gases were obtained respectively). Further, air was passed into the bottle until the total pressure was brought to 1.02*10^5 n/m^2 and a mixture of air and test gas was passed from the bottle through the sorbent tube, creating a vacuum at the outlet of this tube. The entire system was thermostated, for that it was washed with air at a temperature of 278±5, 295±2, 320±2 K. [7, 8]

In the case of the generation of ethanol, acetone, aniline, etc. vapors, a conventional large tube (40 cm^3) is used with a gas outlet tube. A sample of substance is placed in a test tube, a gas outlet tube is connected, then the tube is heated in a water bath, while the substance gradually evaporates, the vapors pass to the sorbent, diffusion and sorption proceeds. Sorption isotherms of a number of toxicants are shown in Fig. 1-3.

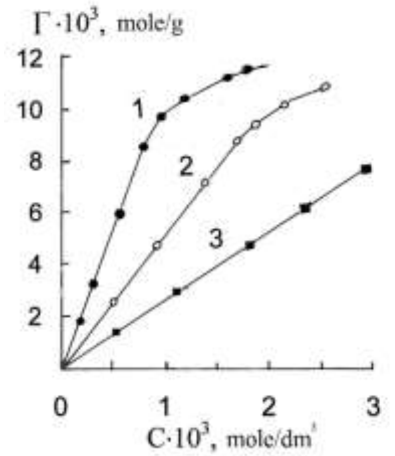

Fig.1. Sorption isotherms of H2S :1 – 335 K, 2 – 323 K, 3 – 298 K

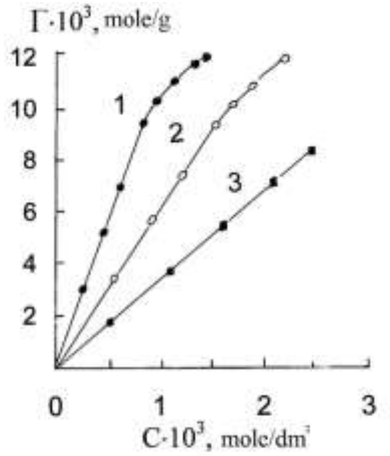

Fig.2. Sorption isotherms of CO2 :1 – 335 K, 2 – 323 K, 3 – 298 K

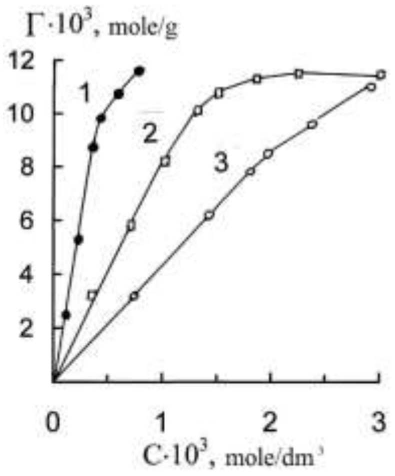

Fig.3. Sorption isotherms of SO2:1 - 335 K, 2 - 323 K, 3 - 298 K

With the use of isotherms (Figures 1-3), the reciprocal values of sorption (1/Γ) and concentration (1/C) were calculated, and the Langmuir isotherms in rectilinear form were scheduled. On the isotherm in the coordinates "1/Γ - 1/C" the straight line cuts off a numerically equal to $\frac{1}{\Gamma_\infty}$ segment on the vertical axis, and the slope of this line is equal to $\frac{1}{\Gamma_\infty \cdot K}$, where K is the sorption constant, Γ_∞ is the limiting sorption, mole / g.

The obtained results were used to calculate the thermodynamic and equilibrium sorption characteristics of a number of toxicants on the sorbent (Table 3). [9,10,11]

Table 3. The main sorption and thermodynamic characteristics of sorbate - sorbent systems

SORBATE	SORPTION CONSTANTS K·10-2			$-\Delta H$, kJ/ mole	$-\Delta G_{295}$, kJ/ mole	ΔS, kJ/ mole	$G_{\infty 295}$, g/g
	K_{295}	K_{323}	K_{335}				
SO_2	1,0	3,70	20,0	61,50	1,129	17,05	0,64
H_2S	1,50	4,10	25,0	57,71	1,220	15,43	0,30
CO_2	1,30	4,25	25,50	61,13	1,190	16,69	0,35

Given in Table 2 results make it possible to draw an unambiguous conclusion, that the chemisorption process proceeds very fully.

CONCLUSION

Thus, the sorbent, when in the large particles form has a large specific surface, which makes it possible to use it to trap toxicants from water and air, while the sorption characteristics of the latter remain at a high level.

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