SECTION 3

PHYSICS OF RADIATION AND ION-PLASMA TECHNOLOGIES

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IODINE SORPTION CAPACITY OF CARBON FIBER CLOTH MATERIALS AND GRANULAR ACTIVATED CARBONS

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The sorption capacity for iodine vapors of samples of carbon fiber cloth materials 31-3, 31-6, 35-1, 35-2, and KIPT 16-00 obtained at NSC KIPT, carbon fiber cloth materials of the Saut and Busofit brands and active granular carbons ISQ-3, SKT-3, and DGF-2 has been studied. The sorption capacity of carbon fiber cloth materials of series 31-6 and KIPT 16-00 is ~ 30% higher in comparison with Saut fiber cloth and ~ 4 times higher than the characteristics of active granular carbons SKT-3 and DGF-2 it has been shown.

INTRODUCTION

Sorbents are characterized by absorption capacity - adsorption capacity corresponding to the amount of adsorbed adsorbate per unit mass or unit volume. The adsorption capacity of the sorbent determines the service life of devices for cleaning the environment from harmful impurities. In the ventilation systems of nuclear power plants, filters-adsorbers with granular activated carbons are used, which are effective sorption-filtering materials for cleaning the air environment of the working rooms of nuclear power plants from radioactive molecular iodine, methyl iodide, as well as radioactive inert gases and other volatile substances contained in gas aerosol emissions. At the same time, it is taken into account that the isotope ^{131}I is especially dangerous for humans (half-life is 8.5 days), which is due to its biochemical identity with stable iodine, which plays a vital role in the body, selectively accumulating in the thyroid gland.

Sorbents in the form of granular activated carbons, which can be used in the manufacture and repair of filter-adsorbers for the needs of Ukrainian NPPs, must have high values of a number of characteristics, including the adsorption capacity for iodine and methyl iodide [1]. This characteristic essentially depends on the manufacturing technology, porosity, and specific surface area. There is a wide range of granular active carbons on the market, but at the same time, new promising sorbents are being researched in a number of countries. These materials include carbon fiber cloth, the production technology of which was developed at the NSC KIPT.

It has now been established that activated carbon is characterized by a specific interaction with water vapor. As a result of the technological procedure of steam activation on the surface of coal crystallites, additional oxygen-containing functional groups, Bronsted acids: hydroxyl, carboxyl and phenolic [2] appear. Gaseous media cleaned from harmful impurities, as a rule, contain water vapor. Water molecules are sorbed mainly on the above active sites, forming hydrogen bonds with them, as shown in works on IR spectroscopy [3]. The nonspecific interaction of water with the surface of activated carbon is weak due to its low ability to polarize. On the basis of structural analysis in combination with direct measurement of sorption isotherms, it was established [4] that water, sorbed on edge defects, changes the interplanar distances and the size of the basal crystallite faces. In fine pores, a water molecule can form a sorption complex simultaneously with several surface acid sorption sites. There is every reason to believe that such features of the interaction of water molecules with active carbon will also be characteristic of activated carbon fiber clothes. Therefore, when determining the adsorption characteristics of activated carbon and carbon fiber cloth by iodine in real conditions (air with water vapor and an admixture of an adsorptive - in this case, iodine), it is necessary to consider the absorption factor of water vapor.

The specific surface area is one of the important characteristics of sorbents. When comparing certain types of them (in particular, activated carbons or carbon fiber clothes obtained from different raw materials or using different methods), the measurement results of the specific surface makes it possible to correlate morphology of micropores with sorption properties of carbon fiber clothes and granular activated carbons from various manufacturers. Considering the above, the purpose of the work was determined: a comparative study, considering the factor of the presence of water vapor in the air, the adsorption properties of iodine and the specific surface of some carbon materials.

SAMPLES AND EXPERIMENTAL METHOD

SAMPLES

Investigated samples of granular activated carbons of the following brands: DGF-2 diameter d = 2.0...2.5 mm, length l = 4...6 mm; SKT-3 – d = 2.5 mm, l = 4...8 mm; ISQ-3 – d = 3 mm, l = 4…8 mm.

The activated carbon fiber cloth of the NSC KIPT were obtained by the method of sequential carbonization and activation of woven materials. The fabric "Bresent suroviy H/B/ Jute (470)" and cotton fabric for waffle towels were used as precursors. The activation and carbonization of these fabrics was carried out on pyrolysis units of the AGAT type using technological attachments based on carbon-carbon composite materials. The processes were carried out in an argon atmosphere. The article discusses the results obtained in carbonization processes without the use of fire retardants, catalysts and other auxiliary reagents.

The design of the reactor is made in such a way that conditions close to isothermal are realized inside. Temperature control and maintenance is carried out using a thermocouple introduced through one of the holes in the heater directly into the internal volume of the reactor. Samples in the form of cuts were placed on the central rig. In one process, from 1 to 6 samples were processed. In the case of a process with several samples, they were numbered from the central tube.

Carbonization and activation of the carbon fiber cloth was carried out according to the temperature rise schedule shown in Fig. 1. At the first stage – heating and carbonization of the fabric in an argon atmosphere up to a temperature of 1000 °C in 6 h, at the second – activation at 1000 °C for 90 min with the addition of water.

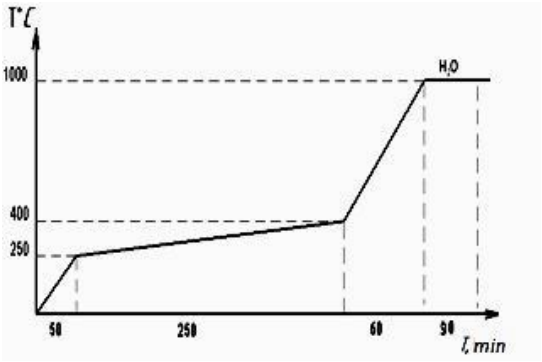

Fig. 1. Temperature rise graph

The volume of water used in the activation process is 200 ml. The yield of activated carbon fiber clothes is 12…20% by weight, depending on the number of samples in one process, which, as a result of the gradient upon activation, differ in properties. In this work, samples of carbon fiber cloth obtained on the basis of the fabric "Bresent suroviy H/B/ Jute (470)" 31-3.31-6.36-1.35-2 are investigated, where the first index is the process, and the second is the location of the sample from the central rod of the rig, as well as a sample obtained from a fabric for waffle towels (sample 16-00).

Samples of carbon fiber cloth materials of the Busofit and Saut brands produced by OJSC "SvetlogorskKhimvolokno", Belarus, are produced by an industrial method by carbonization and activation of viscose woven precursors. According to the specification, the active surface for iodine for Saut is at least 105%, and for Busofit it is in the range 110…140%, and the specific surface for BET for Busofit is 500…1500 m^2/g, and for Saut it is 2000 m^2/g.

METHOD FOR DETERMINING THE ADSORPTION CAPACITY OF SORBENTS

In our experiments, to measure adsorption, we used a special stand (Fig. 2), consisting of two desiccators (1), (9) with samples of adsorbents in weighing boxes (4), (11).

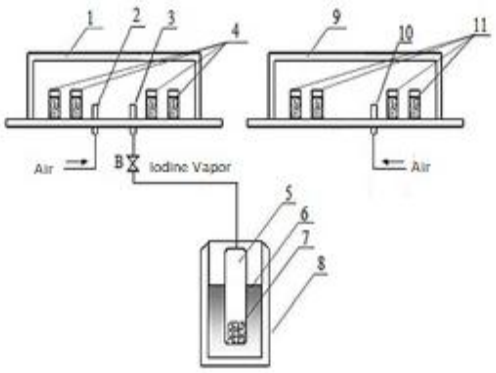

Fig. 2. Scheme of the stand for measuring the absorption of iodine vapor by sorbents in the presence of atmospheric air with water vapor: 1, 9 – desiccators; 2, 10 – underwater tubes; 3, 11 – containers with an adsorbent; 5 – ampoule; 6 – thermostatic medium; 7 – crystalline iodine; 8 – Dewar vessel; B – valve

Desiccators communicated with the atmosphere through pipes (2), (10). The first desiccator was connected through a valve to an iodine vapor generator consisting of a thermostat in the form of a Dewar vessel (8) with a thermostating medium and an ampoule (5) with crystalline iodine (7). As a result, in the first desiccator, adsorbent samples absorbed iodine vapor, the partial pressure of which corresponded to the temperature of crystalline iodine in the thermostat, and water vapor present in the air at atmospheric pressure. At the same time, in the second desiccator, the control samples of adsorbents interacted only with atmospheric air containing water vapor.

Samples of the studied sorbents (~ 10 g in weight) were weighed on an AS220/C balance and placed in weighing vessels, which were installed in desiccators. The adsorption of iodine occurred at a temperature of 20 °C, atmospheric air pressure, and a partial iodine vapor pressure of 0.17 Torr. During the experiment, the samples were periodically weighed; the temperature and humidity of the air in the room were measured.

According to the measurement results, the relative change in the mass of the sorbents was determined:

$$\left(\frac{\Delta m}{m_0}\right)_{I_2} = \left(\frac{\Delta m}{m_0}\right)_{I_2+H_2O} - \left(\frac{\Delta m}{m_0}\right)_{H_2O}. \quad (1)$$

The first term in (1) corresponds to the increase in the mass Δm of the sorbent in the first desiccator due to the absorption of I_2 vapors together with water vapor in the air; the second characterizes the control sample in the second desiccator, which interacted only with an air medium containing water vapor.

METHOD FOR DETERMINING THE SORBENTS SPECIFIC SURFACE AREA

The Brunauer, Emmett, and Tayler method (BET method) is one of the most proven methods for

determining the specific surface area for adsorbents with a certain type of adsorption isotherm [5]. To determine the specific surface area of the adsorbent, only the initial portion of the adsorption isotherm is used in the pressure range from 50 to ~ 200 Torr. Gaseous nitrogen served as the adsorbate. For a more accurate determination of specific surface area, a reference sample with a well-known specific surface area was used. The specific surface area was determined by the formula:

$$S = \frac{Sr \cdot m_r}{m_s}\left(\frac{\Delta Ps - \Delta Po}{\Delta Pr - \Delta Po}\right), \quad (2)$$

where m_s – sample weight; m_r – reference weight; S_r – specific surface area of the reference; ΔPs, ΔPr, ΔPo – the difference in pressure at room temperature and the temperature of liquid nitrogen in the chamber of the device with a sample, a standard and for an empty device, respectively. The possible error in determining the specific surface area within the BET model is mainly associated with the error in determining the pressure. Calculations and experiments have shown that the relative error is 7…10%.

The scheme of the stand for determining the specific surface area is shown in Fig. 3.

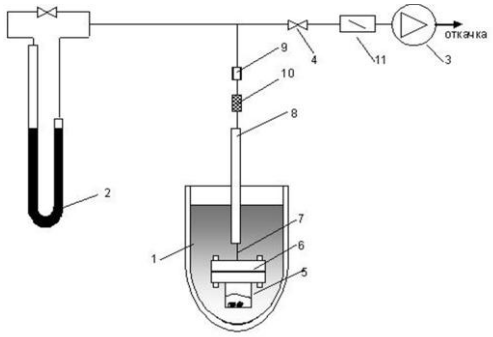

Fig. 3. Measuring device scheme: 1 – Dewar with liquid nitrogen (cryostat); 2 – mercury differential manometer (pressure measurement system); 3 – foreline pump; 4 – gas inlet valve; 5 – measuring chamber; 6 – measuring chamber cover; 7 – supply capillary; 8 – vacuum jacket; 9 – connector; 10 – filter; 11 – nitrogen trap

The stand consists of the following units: a cryostat 1, a pressure measurement system 2, a pumping system 3, 11, a gas inlet valve 4. The cryostat is a metal Dewar vessel in which a measuring chamber 5 with test sample is placed. The measuring chamber is made of brass in the form of a cylinder with a volume of 22.6 cm^3 and has a removable cover 6 on a flange joint sealed with a fluoroplastic gasket. The cover has a hole for supplying nitrogen gas and pumping out the device. The chamber is connected to the pressure meter 2 by a nickel silver capillary 7, which is surrounded by a vacuum jacket 8. For the convenience of loading the test sample and assembling the working chamber, there is a detachable connection 9 in the warm part, with which the chamber can be disconnected from the device. Filter 10 serves to prevent sample particles from entering the pressure measurement system. It is made in the form of a disk 2 mm thick from vacuum sintered copper powder with a particle size of ~ 10 μm and a porosity of about 50%. The pressure in the system is measured using a differential mercury manometer, which is connected to the instrument with a copper capillary. In order to reduce the volume of the warm part of the device, one elbow of the differential manometer and all connecting pipes are made of a capillary with an inner diameter of 1 mm. The device is evacuated by a foreline pump 3 with a nitrogen trap 11. The operating temperature is achieved using liquid nitrogen poured into the cryostat.

Before measurements, the sorbent samples were heated at T = 300 °C for 2 h at a pressure of ~ $1 \cdot 10^{-1}$ Torr, which ensured complete moisture removal.

RESULTS

On Fig. 4 is shown the dependences of the increase in the mass of sorbents due to the adsorption of iodine, calculated by formula (1). The duration of the first (see Fig. 4,a) and second (see Fig. 4,b) series of experiments was 90 and 100 days, respectively.

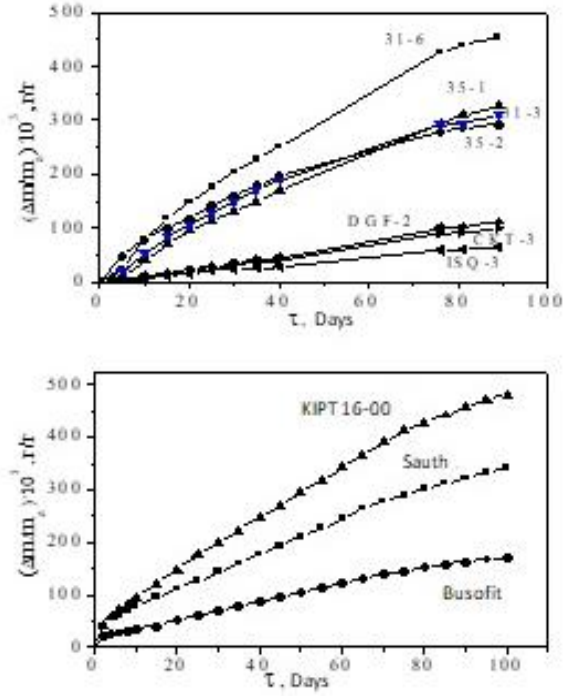

Fig. 4. The dependence of the adsorption value of molecular iodine on the duration of the adsorption process for various sorbents

The carbon fiber cloth materials of the KIPT 16-00, 31-3, 31-6, 35-1, and 35-2 series are characterized by a higher sorption capacity compared to activated carbons. For these tissues, the dependences of $\Delta m/m_a$ on t can be divided into three stages of the sorption process. The first stage ($t \le 10$ days) of the most intense sorption rate is replaced by a rather long second stage, almost linear at $20 < t \le 80$, for which a noticeable decrease in the sorption rate is typical. The third stage ($t > 80$ days) can be characterized as a precursor to the release of sorption to saturation. It should be noted that carbon fiber cloth samples from KIPT 16-00 and 31-6 have the maximum absolute values of iodine sorption: $\Delta m/m_a$ = 460…470 mg/g.

The results of calculating the specific surface area of the samples S according to formula (2) and the maximum values of sorption $(\Delta m/m)_{max}$, estimated from Fig. 2, are presented in Table.

The values of specific surface area and maximum values of sorption of carbon fabrics and granular activated carbons

Sample	S, m^2/g	$(\Delta m/m)_{max}$, mg/g
Carbon fiber cloth		
31-6	892±90	460
35-1	1167±116	370
31-3	683±70	300
35-2	790±80	280
KIPT 16-00	805±80	470
Sauth	983±90	350
Busofit	407±40	160
Granular activated carbon		
DGF-2	1200±120	110
СКТ-3	1040±100	100
ISQ-3	600±60	70

From a comparison of the data in Table, we can conclude the following.

1. In the series of granular active carbons ISQ-3, DGF-2 and SKT-3, the minimum values of sorption and specific surface area are characterized by ISQ-3. DGF-2 and SKT-3 coals have higher values of sorption and specific surface area.

2. The carbon fiber cloth of the Saut and Busofit brands produced by JSC "Svetlogorsk Khimvolokno" are characterized by the values of S ~ 1000 m^2/g and $(\Delta m/m)_{max}$ = 350 mg/g versus S ~ 400 m^2/g and $(\Delta m/m)_{max}$ = 170 mg/g, which may indicate a correlation between the adsorption capacity and specific surface area, similar to granular activated carbons.

3. For carbon fiber cloth materials obtained at NSC KIPT, there is no general correlation between adsorption capacity and specific surface area. So, for samples 31-2 and 31-3 $(\Delta m/m)_{max}$ is 280 and 300 mg/g at S values of 790 and 680 m^2/g. For samples 31-6 and KIPT 16-00, the maximum sorption characteristics (460 and 470 mg/g) were achieved at higher S values (≈ 890 and ≈ 800 m^2/g). The carbon fiber cloth of series 35-1 with a maximum specific surface area S 1170 m^2/g has a lower value of $(\Delta m/m)_{max}$ = 370 mg/g.

4. For sorbents of the same type carbon fabrics - iodine sorption is ~ 30% higher in fabrics of series 31-6 and KIPT 16-00 in comparison with Saut carbon fiber cloth. If we are talking about comparing the sorption capacity of different types of sorbents (activated carbons and carbon fiber clothes), then the data obtained indicate significantly higher (~ 4–6 times) values in carbon fiber clothes obtained at NSC KIPT in comparison with the characteristic's active granular carbons SKT-3, DGF-2, ISQ-3.

On the whole, at lower, in comparison with activated carbons, values of specific surface, carbon fiber clothes obtained at NSC KIPT have a higher adsorption capacity. This can be attributed to the difference in pore morphology and other characteristics of the porous structure, which may be associated with the specificity of the feedstock and the peculiarities of the technology for their production.

CONCLUSIONS

For a series of samples of activated carbon fiber cloth 31-3, 31-6, 35-1, 35-2, and KIPT 16-00, obtained at the NSC KIPT, the values of the sorption capacity for iodine vapor were determined and compared with the characteristics of carbon fiber clothes of the Saut and Busofit brands and granular activated carbons SKT-3, ISQ-3, DGF-2 and SKT-3.

The sorption capacity of samples 31-6 and KIPT 16-00 is ~ 30% higher in comparison with the Saut carbon fiber clothes and is ~ 4 times higher than the characteristics of activated granular carbons SKT-3 and DGF-2 has been shown.

To clarify the prospects for the use of carbon fiber cloth materials, developed at NSC KIPT, as a working material for iodine filters of ventilation systems of nuclear power plants, it is planned to conduct studies of the absorption of methyl iodide, mechanical and aerodynamic characteristics.

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СОРБЦІЙНА ЄМНІСТЬ КАРБОНОВИХ ТКАНЕЙ І СОРТІВ АКТИВОВАНОГО ВУГІЛЛЯ ПО ЙОДУ

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Досліджено сорбційну ємність по парам йоду зразків карбонових тканин 31-3, 31-6, 35-1, 35-2 і ХФТІ 16-00, отриманих в ННЦ ХФТІ, карбонових тканин марок Саут і Бусофіт і сортів активованого гранульованого вугілля ISQ-3, СКТ-3 і DGF-2. Показано, що сорбційна ємність у тканин серій 31-6 і ХФТІ 16-00 на ~ 30% вище в порівнянні з тканиною Саут і в ~ 4 рази перевищує характеристики сортів активованого гранульованого вугілля СКТ-3 та DGF-2.

СОРБЦИОННАЯ ЕМКОСТЬ КАРБОНОВЫХ ТКАНЕЙ И АКТИВИРОВАННЫХ УГЛЕЙ ПО ЙОДУ

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Исследована сорбционная емкость по парам йода образцов карбоновых тканей 31-3, 31-6, 35-1, 35-2 и ХФТИ 16-00, полученных в ННЦ ХФТИ, карбоновых тканей марок Саут и Бусофит и активированных гранулированных углей ISQ-3, СКТ-3 и DGF-2. Показано, что сорбционная емкость у тканей серий 31-6 и ХФТИ 16-00 на ~ 30% выше в сравнении с тканью Саут и в ~ 4 раза превышает характеристики активных гранулированных углей СКТ-3 и DGF-2.