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Technical Note

A method for properties evaluation of activated charcoal sorbents in iodine capture under dynamic conditions

Eldar P. Magomedbekov, Alexander V. Obruchikov*

Department of High-Energy Chemistry and Radioecology, D. Mendeleev University of Chemical Technology of Russia, Moscow, Russia

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ABSTRACT

Experimental equipment for studying the sorption properties of iodine sorbents using radioactive methyliodide has been developed. The sorption capacity index α is proposed as a criterion parameter for assessing the quality of impregnated activated charcoals. It was found that this parameter does not depend on the dynamic conditions during the sorbent test. It was shown that values of the sorption capacity index allow to recommend iodine sorbents for industrial gas cleaning processes.

1. Introduction

The efficiency of radioactive iodine compounds trapping in ventilation and gas purification systems of nuclear power plants (NPP) depends on many factors. The main factor is quality of impregnated activated charcoals. For quality control, as well as for comparison of different sorbents, a standard test method is required. There is also a need for criterion which can be used for exact evaluation of sorption capacity and suitability of the sorbent for application at nuclear power plants. For this purpose, standard test methods based on evaluation of radioactive methyliodide breakthrough through the sorbent layer followed by calculation of either trapping efficiency (E) $CH_3^{131}I$ or decontamination factor (DF) [1, 2] are used.

However, these indicators indirectly characterize the sorbent capacity to trap radioiodine under dynamic conditions. This is due to the fact that the breakthrough process depends on the grain size of the sorbent, the length of the sorption layer, the linear velocity of the gas flow. In addition, results of trapping efficiency and purification factor evaluation are often uncertain because of the small amount of methyliodide penetrated through the layer. The comparison of such test results for activated charcoals gives ambiguous conclusions regarding the sorbent quality.

Nowadays, an approach for defining the quality of iodine sorbents by means of the sorption capacity index and the iodine sorbent standard test method has been developed [3–5]. However, in test reports, often the quality criteria are still DF or E. The goal of this paper is to show advantages and independence of the sorption capacity index from dynamic test conditions and to give recommendations on the index implementation.

2. Material and methods

For studying of sorption properties and also for quality control of iodine sorbents used at nuclear power plants, an experimental facility that allows to use radioactive iodine was developed, manufactured and certified (Fig. 1). The basis of the development was an ability to analyze design features of plants described in a number of papers [6–9]. As a result, the facility provides the following test conditions:

Temperature	up to 60°C;
Relative humidity of gas flow	up to 95%;
Linear gas velocity in the tested column	up to 0.2 m/sec;
Specific volume activity of methyliodide ($CH_3^{131}I$)	from 10^3 to 10^6 Bq/m^3;
$CH_3^{131}I$ concentration in the gas flow	from 5 to 60 mg/m^3.

* Corresponding author. Miusskaya sq. 9, 125047, Moscow, Russia.
E-mail address: alexobruch@mail.ru (A.V. Obruchikov).

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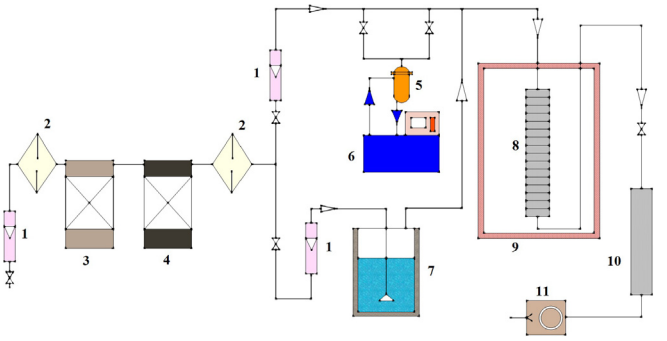

Fig. 1. Simplified scheme of experimental facility. 1 – rotameter; 2 – aerosol filter; 3 – column with zeolite; 4 – column with activated carbon; 5 – $CH_3^{131}I$ evaporator; 6 – circulation thermostat; 7 – gas flow humidifier; 8 – column with sorbent; 9 – dry-air thermostat; 10 – column with silica gel; 11 – diaphragm pump.

It can be seen in Fig. 1 that the experimental facility consists of several sections.

In the carrier-gas preparation section, preliminary drying of atmospheric air is performed in the column [3] filled with 2 L of synthetic zeolite NaA (grain size 4.5 ± 0.5 mm). Also the gas purification from impurities presented is carried out in the column [4] with 2 L of activated charcoal (grain size 3.0 ± 0.5 mm). The gas flow rate is measured using AWM5000 Series [1] airflow sensors (Honeywell). Standard AFA-type aerosol filters [2] are used to purify the gas stream from solid aerosols. This section also includes a vacuum system, which works during zeolite and activated charcoal regeneration after heating up to 300–350 °C. The gas humidification section is designed to provide and maintain a predetermined relative humidity of the gas flowing to the sorbent test section. The main element of the section is a bubble type humidifier [7]. The sorbent test section is located in a fume hood and consists of the methyliodide evaporator [5] and the sorbent test column [8] located in a dry air thermostat [9]. The evaporator has been developed at the D. Mendeleev University of Chemical Technology of Russia. The constant evaporation rate of CH_3I is provided by the thermostatting [6] of the cuvette at 20°C. The stainless steel column [10] with inner diameter of 30.0 ± 0.1 mm and height of 250 mm is used to determine the radioiodine breakthrough. The purified air is supplied into the fume hood with the MPC (Welch) chemical resistant diaphragm pump (11).

Previous use of metal evaporators for methyliodide showed that even high-quality stainless steel is subject to corrosion over time. The radioactive methyliodide evaporator is made of corrosion–resistant material – polytetrafluoroethylene (Teflon or PTFE-4). Structurally, the six part device assembly is shown in Fig. 2.

The test column (Fig. 3) with inner diameter of 30.0 ± 0.1 mm was used in the experiments. The column is divided into compartments (Fig. 4) with height of 10.0 ± 0.1 mm each and is made of corrosion resistant material, easily deactivated. The charcoal sorbent was filled into every compartment. Thus, the total height of the sorbent could be regulated by the number of compartments placed on top of each other. Distribution of radioactive methyliodide along the sorbent layer was measured in compartments of dismountable column by means of scintillation gamma spectrometer (sodium iodide-based detector). The value of radioiodine breakthrough was measured in the protective column (Fig. 1, item 10) with silica gel (grain size 2.0 ± 0.2 mm) containing 8% of silver nitrate. The activity of radioiodine was counted at the energy of 364 keV. It should be noted that measurements of the activity of charcoal compartments and silica gel were carried out at the same counting geometry.

In this paper, samples of industrial sorbent VSK-5IK (Russia,

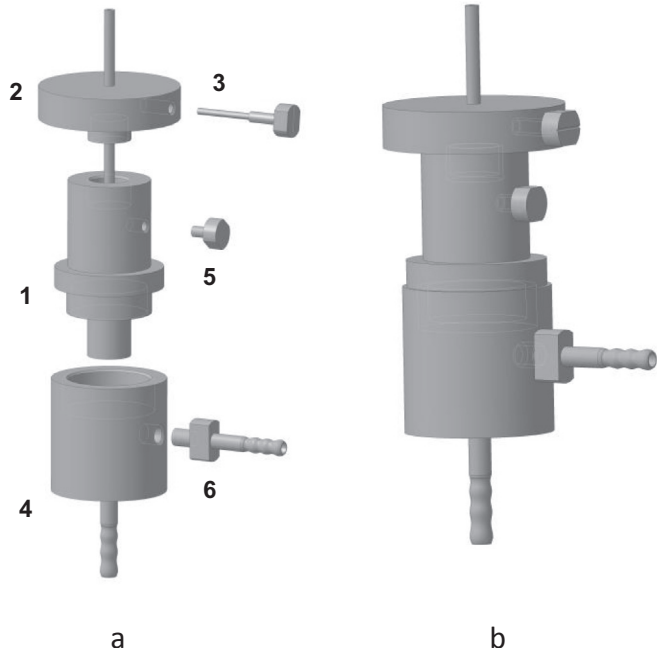

Fig. 2. View of radioactive methyliodide evaporator: a – individual parts (1 – cuvette with liquid methyliodide, 2 mL volume; 2 – threaded sealing cap; 3 – element for methyliodide vapors cutoff with capillary tube; 4 – thermostating compartment for reservoir; 5 – threaded plug; 6 – threaded output brunch for water); b – evaporator assembly.

activated charcoal for NPP, containing up to 1.2% triethylenediamine and 1.2% potassium iodide) were used to study the sorption capacity. All tests were carried out under the following conditions: temperature – 30.0 ± 0.1 °C and relative humidity of the flowing gas – 90.0 ± 1.5%. Concentration of $CH_3^{131}I$ was maintained at a level of 25 ± 7 mg/m^3. The moist air passed through the samples for 16 h prior to the experiments with I-131 in order to eliminate any effects of the adsorption heat of the water vapors on the sorption of methyliodide. Then the duration of $CH_3^{131}I$ supplying was 3 h according to [4].

The decontamination factor (DF) and the trapping efficiency (E) were calculated using the following equations:

$$DF = \frac{A}{B} \tag{1}$$

$$E = \left(1 - \frac{1}{DF}\right)100\% \tag{2}$$

where A – total activity of radioiodine injected into the gas flow, Bq; B – total activity of radioiodine in protective column (breakthrough), Bq. It should be noted that the total activity injected into the gas flow was calculated as the sum of the activities of all compartments with activated charcoal and silica gel in the protective column, taking decay correction into account.

At the initial stage, two size fractions of activated charcoal VSK-5IK were selected by sieve analysis: 1.0–2.0 mm and 2.0–3.0 mm (see Table 1). Portion of free volume in the bulk sorbent layer was $\chi = 0.23 \pm 0.01$ and $\chi = 0.32 \pm 0.01$, respectively [4]. Using this parameter, it is possible to evaluate the free volume of air (V_{fv}) in the bulk layer (V_s) [5]. To estimate impact of the sorbent layer height on the $CH_3^{131}I$ removal efficiency, comparative tests were carried out in the 100, 150 and 200 mm test columns. Linear velocity of the gas flow in all three cases was 18.2 cm/s. At the second phase of testing, effect of the sorbent grain size on methyliodide

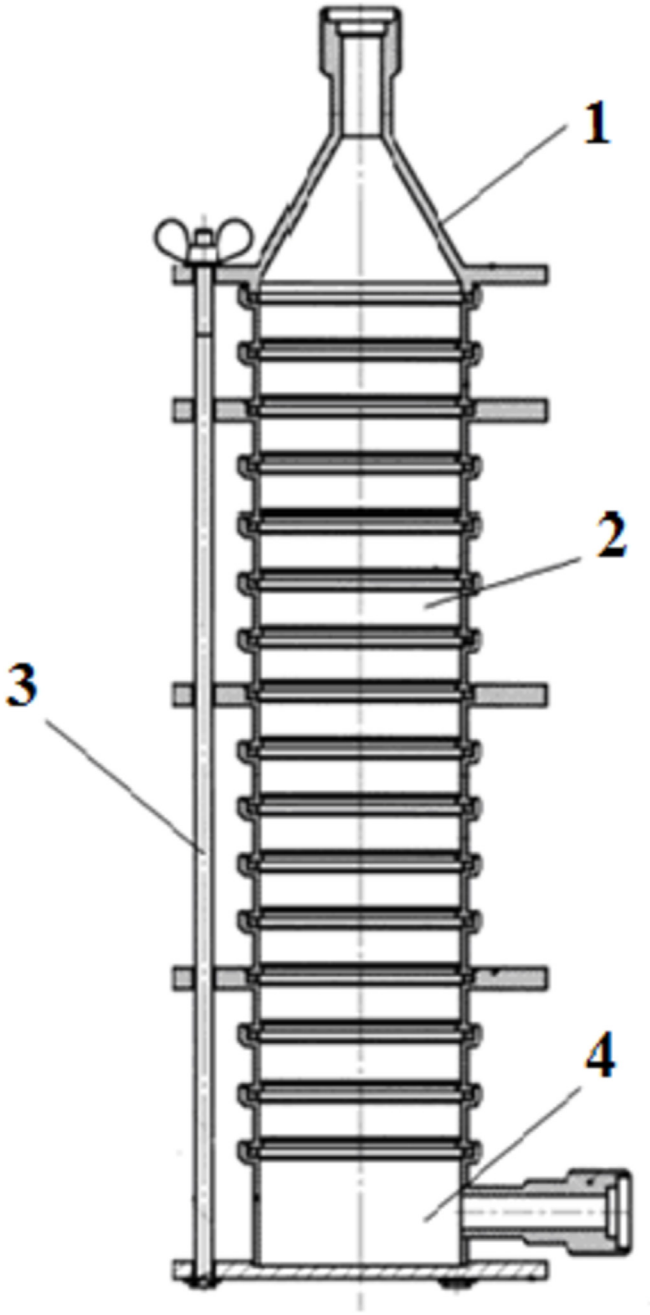

Fig. 3. The test column. 1 – removable cover with an inlet branch pipe; 2 – compartment with the sorbent; 3 – directing rod; 4 – bottom with outlet branch pipe.

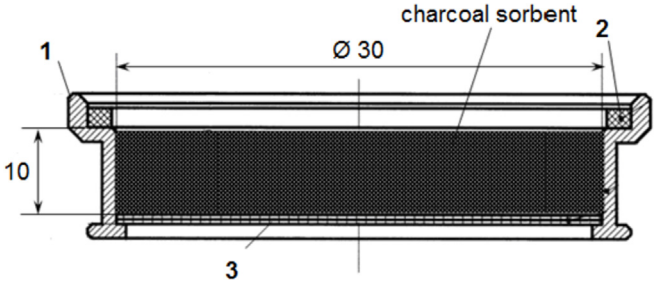

Fig. 4. The column compartment with sorbent. 1 – case; 2 – O-ring seal; 3 – perforated partition with a grid.

trapping efficiency was studied. For this purpose, previously selected activated charcoal fractions were loaded into the 150 mm column. Dependency assessment of sorption efficiency on the gas flow velocity was carried out within the third series of tests. The fraction of 1.0–2.0 mm grain sizes was selected for the test; the activated charcoal height in the column was 150 mm.

3. Results and discussion

The radioiodine distribution along the sorbent layer and calculated results of purification degree and decontamination factors are shown in Table 2.

As it can be seen from presented data, the dynamic conditions of sorbent tests essentially affect the final values of parameters of radioactive iodine removal efficiency. More efficient purification is obviously due to increased time of the gas contact with the activated charcoal.

For any sorbent, the amount of the absorbed material, including radioactive iodine, is determined by the contact time between the gas flow and the sorbent. The contact time (τ_c) is the parameter that shall be used to establish a criterion characterizing the sorbent efficiency. In paper [3] the sorption capacity index (α) was proposed to be such a criterion. The α index shows the extent to which the radioactive component content in the gas flow decreases after 1 s of its presence in the volume of sorbent.

The α index was calculated according to experimental data using a formula:

$$\ln\frac{A}{A-A_x} = \alpha\chi\frac{L}{U} \tag{3}$$

where A_x – total activity of radioiodine at length x of sorbent layer ($x \rightarrow L$), Bq; χ – portion of free volume (V_{fv}) in the full volume occupied by the sorbent (V_s) which depends on the size and shape of granules of activated charcoal $\chi = \frac{V_{fv}}{V_s}$; L – total length of the sorbent layer, cm; U – linear gas velocity in full cross section of the column, cm/s. It is obvious that the member $\chi\frac{L}{U}$ reflects actual time τ_c of gas flow contact with the sorbent.

One of the assumptions on which the proposed method is based is the exponential dependence of the distribution of methyliodide concentration along the sorbent layer [3]. Therefore, to determine the α value, it is not necessary to know how much radioactive methyliodide has passed through the layer being tested (the breakthrough value). The only requirement is to measure the activity distribution along the layer of iodine sorbent to verify that it is exponential.

As a result of experimental data processing, the sorption capacity indices for all tested VSK-5IK samples were calculated (Table 2). To do this, dependences $\ln\frac{A}{A-A_x} = f(\tau_c)$ were plotted and α was calculated as a slope of the straight line (Fig. 5).

It can be seen that the α index does not depend on the test conditions in the study and is equal, on average, to $19.94 \pm 0.04\ s^{-1}$. In other words, this parameter characterizes only the properties of the sorbent itself and can be used to assess its quality. True contact time is calculated based on the fraction of free volume (χ) in the bulk activated charcoal layer [5].

The sorption capacity indices, which can be easily determined for the sorbent use at nuclear power plants, are defined based on the IAEA recommendations, which specify that radioactive methyliodide content in gaseous radioactive wastes should be reduced by at least 100 times [2]. This means that the $CH_3^{131}I$ trapping efficiency from the gas flow should be more than 99%. Obviously, this condition is met for the value $\ln\frac{A}{A-A_x} = \ln 100 = 4.605$. Minimum indices α_{min} are limiting values for any sorbent and do not depend

Table 1
Results of VSK-5IK sieve analysis.

Grain size, mm	<0.5	0.5–1.0	1.0–1.6	1.6–2.0	2.0–2.5	2.5–3.0	3.0–3.5	>3.5
Relative ammount, %	0.0	1.2	14.1	19.1	31.9	24.2	9.4	0.1

Table 2
Calculated values of $CH_3^{131}I$ sorption efficiency versus the test conditions.

Test number	1	2	3	4	5	L, mm
	Radioiodine distribution along the sorbent layer, kBq					
Gas velocity, cm/sec	9.1	18.2	18.2	18.2	18.2	
Grain size, mm	1.0–2.0	1.0–2.0	2.0–3.0	2.0–3.0	2.0–3.0	
	4.39 ± 0.13	5.48 ± 0.17	7.04 ± 0.21	4.32 ± 0.13	5.82 ± 0.17	10
	2.65 ± 0.08	4.26 ± 0.13	4.96 ± 0.15	3.04 ± 0.09	4.10 ± 0.12	20
	1.60 ± 0.05	3.31 ± 0.10	3.49 ± 0.10	2.14 ± 0.06	2.89 ± 0.09	30
	0.971 ± 0.029	2.58 ± 0.08	2.46 ± 0.07	1.51 ± 0.05	2.03 ± 0.06	40
	0.587 ± 0.018	2.00 ± 0.06	1.73 ± 0.05	1.061 ± 0.032	1.43 ± 0.04	50
	0.355 ± 0.011	1.56 ± 0.05	1.220 ± 0.037	0.747 ± 0.022	1.008 ± 0.030	60
	0.215 ± 0.006	1.209 ± 0.036	0.859 ± 0.026	0.526 ± 0.016	0.710 ± 0.021	70
	0.130 ± 0.004	0.940 ± 0.028	0.605 ± 0.018	0.371 ± 0.011	0.500 ± 0.015	80
	0.078 ± 0.004	0.730 ± 0.022	0.426 ± 0.013	0.261 ± 0.008	0.352 ± 0.011	90
	0.047 ± 0.003	0.568 ± 0.017	0.300 ± 0.009	0.184 ± 0.006	0.248 ± 0.007	100
	0.029 ± 0.003	0.441 ± 0.013	0.211 ± 0.006	0.129 ± 0.004	–	110
	0.017 ± 0.003	0.343 ± 0.010	0.149 ± 0.004	0.091 ± 0.004	–	120
	0.010 ± 0.003	0.266 ± 0.008	0.105 ± 0.004	0.064 ± 0.003	–	130
	0.006 ± 0.002	0.207 ± 0.006	0.074 ± 0.004	0.045 ± 0.003	–	140
	0.004 ± 0.002	0.161 ± 0.005	0.052 ± 0.003	0.032 ± 0.003	–	150
	–	–	0.037 ± 0.003	–	–	160
	–	–	0.026 ± 0.003	–	–	170
	–	–	0.018 ± 0.003	–	–	180
	–	–	0.013 ± 0.003	–	–	190
	–	–	0.009 ± 0.003	–	–	200
Breakthrough, kBq	0.006 ± 0.002	0.516 ± 0.015	0.018 ± 0.003	0.074 ± 0.004	0.587 ± 0.018	
DF	1850 ± 110	47.6 ± 2.9	1320 ± 80	197 ± 12	33.5 ± 2.0	
E, %	99.94 ± 0.01	97.89 ± 0.13	99.92 ± 0.01	99.49 ± 0.03	97.02 ± 0.18	
Sorption capacity index α, sec^{-1}	19.89 ± 0.01	19.95 ± 0.01	20.00 ± 0.01	19.96 ± 0.01	19.92 ± 0.01	

Notes: L – total length of the sorbent layer, cm; DF – decontamination factor; E – trapping efficiency.

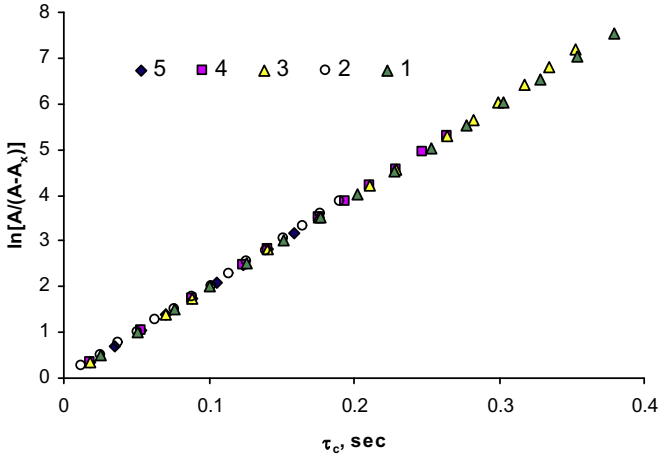

Fig. 5. Comparative data for calculation of sorption capacity index; test number – 1–5; equations used to fit data: 1 – y = 19.89× (R^2 = 0.9999); 2 – y = 19.95× (R^2 = 0.9999); 3 – y = 20.00× (R^2 = 0.9997); 4 – y = 19.96× (R^2 = 1); 5 – y = 19.92× (R^2 = 1).

on temperature and humidity of the gas medium. The values can be easily calculated from the following equation: $\alpha_{min} = \frac{\ln 100}{\tau_c}$. Consequently, a sorbent having the sorption capacity index below specified values at contact time τ_c cannot be recommended for use in iodine decontamination devices (Table 3).

Taking into account that the contact time in NPP charcoal absorbers [10] is usually 0.25 s or more, the minimum value of sorption capacity index will be 18.4 s^{-1} (in accordance with Table 3). Thus, the industrial sorbent VSK-5IK with α larger than the value above may be recommended to remove radioiodine from ventilation paths of plant work premises.

Table 3
Minimum values of sorption capacity index for iodine sorbents.

τ_c., sec	0.20	0.25	0.30	0.35	0.40	0.45	0.50
α_{min}. Sec^{-1}	23.0	18.4	15.3	13.1	11.5	10.2	9.2

Notes: τ_c – contact time of gas flow with the sorbent; α_{min} – minimum value of sorption capacity index.

Several samples of impregnated activated charcoals were tested in paper [3] under the conditions described above. The sorption capacity indices were obtained in a wide range from 8.8 to 31.3 s^{-1}. It is noted that the α index usually grows with increasing amount of impregnant in the sorbent. Nevertheless, one should pay attention to the quality of impregnants, the preparation process of the sorbent, the activated charcoal brand, and the aging of the charcoal sorbent. All these aspects can have a significant effect on the sorption capacity of impregnated charcoals.

A potential capacity of iodine filter can be evaluated in two ways. For devices under design, a sorbent with the experimentally defined α index should be selected. After that, the appropriate gas contact time (τ_c) is defined according to Table 3, using α as a minimum value. Next, the free volume (V_{fv}) for required iodine filter

capacity (Q_f) is calculated by formula $V_{f_v} = Q_f \cdot \tau_c$. Finally, according to the data on the sorbent grain size, the portion of free volume (χ) should be defined and the minimum required volume or height of the sorbent layer should be calculated. For existing and used at NPP iodine filters, actual contact time should be defined using data on the sorbent volume and the calculated portion of free volume. Based on the contact time, recommendation should be made on the use of a sorbent with such an α, at which necessary efficiency of radioiodine removal from gaseous radioactive wastes is ensured.

4. Conclusion

Based on the results of the study, both the trapping efficiency values (E) and the decontamination factors (DF) of methyliodide were calculated. As can be seen from the presented data, the sorbent test conditions significantly influence the values of the radioactive iodine removal efficiency parameters. Obviously, more effective cleaning is due to an increase in the time of contact of the gas with activated charcoal. Thus, neither the decontamination factor nor the trapping efficiency can unambiguously characterize the sorptive capacity of the iodine sorbent.

Based on the data on the distribution of radioactive iodine along the sorbent layer, the sorption capacity indices (α) were calculated. It is shown that the sorption capacity index does not depend on the sorbent test conditions in the study, what makes this criterion a universal parameter for any sorbent characterization. The average value of the α index for all tests performed in the study was $19.94 \pm 0.04\ s^{-1}$ and as a result the VSK-5IK charcoal is applicable for the radioiodine removal at nuclear power plants according to the IAEA recommendations. It should be noted that the research was conducted in the limited experimental conditions. Therefore, for more detailed findings, the additional tests are required. A relatively simple method based on the α index values was proposed to compare industrial sorbents and their ability to adsorb gaseous radioactive waste.

Acknowledgement

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