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Technical Note

Radioiodine removal from air streams with impregnated UVIS® carbon fiber

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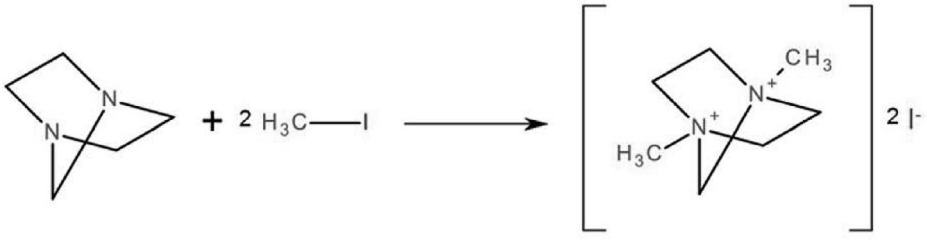
ABSTRACT

This study is devoted to the ability of carbon fiber material samples impregnated with various amounts of barium iodide and triethylenediamine to remove radioactive methyliodide from air streams. The main sorption characteristics of impregnated UVIS® carbon fiber were determined and the use of this material for purifying of technological gas flows at nuclear power plants was evaluated. The methyliodide trapping efficiency by samples impregnated with barium iodide, TEDA, and their mixture was 83.4 ± 0.8%; 93.1 ± 0.6% and 93.5 ± 0.7% respectively, under the same conditions. The study established a significantly higher capacity (8.3 ± 0.07 mg/cm^2) of samples impregnated simultaneously with both chemical compounds toward methyliodide. Under the same test conditions, the values of this parameter for the samples impregnated separately with TEDA and BaI_2 were 2.85 ± 0.05 mg/cm^2 and 0.86 ± 0.04 mg/cm^2, respectively.

1. Introduction

During the operation of nuclear power plants (NPPs), it is inevitable that radioactive fission products from fuel elements will enter the main coolant circuit of the reactor. At the same time, part of the contaminated primary coolant, so – called uncontrolled leaks, get on the floor of production facilities, and their gaseous fission products get into the air of these production areas. The main danger for nuclear power plant personnel and the population is represented by radioactive forms of iodine – primarily the most difficult to trap form of methyliodide (CH_3I) [1,2]. The sorbents based on impregnated activated carbon have been widely used for its localization in the normal operation of nuclear power plants [3–5]. Metal iodides, silver nitric acid, triethylenediamine (TEDA), hexamethylenetetramine (urotropine) and others are often used for their impregnation [6,7]. It is known that the mechanism of radioiodine capture by sorbents containing metal iodides is isotope exchange [8,9]:



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$$CH_3^{131}I_{(g)} + K^{127}I_{(ads)} \leftrightarrow CH_3^{127}I_{(g)} + K^{131}I_{(ads)} \quad (1)$$

Methyl iodide chemically binds to tertiary amines and is practically irreversibly retained in the sorbent [6]:

The charcoal application for radioiodine sorption is associated with the formation of coal dust, which is partially carried away, and partially remains in the adsorber, clogging the channels between the granules and thereby dramatically increases the hydraulic resistance. Removal of dust containing radionuclides from the adsorber requires the installation of an additional aerosol filter that increases the cost of manufacturing and operating the gas purifying system. Currently, a number of materials are known for radioiodine sorption based on glass fibers, polypropylene and carbon fibers [10–12] containing finely ground impregnated activated carbon. The disadvantages of such materials are that the small particles of activated carbon are weakly fixed on the surface of the fibers that leads to the formation of dust and its gradual removal from the sorption material during operation.

From our point of view, a promising way to obtain an iodine sorbent would be to apply chemical compounds that increase the methyliodide trapping efficiency to a microporous carrier devoid of the activated carbon disadvantages. One of these materials can be UVIS® carbon fiber (Uvicom Co Ltd., Mytischi, Russia) obtained by the method of viscose threads carbonation. The main purpose of this study is to assess the sorption capacity of this carbon-fiber material samples impregnated with various compounds in relation to the radioactive methyliodide.

2. Material and methods

The basis for obtaining the sorption material was UVIS® carbon fiber, which is a 0.5 mm thick twill fabric. Data on nitrogen adsorption obtained at the Quadrasorb SI unit allowed determining the specific surface area and total micropores volume of the studied material, which were 806 m^2/g and 0.557 cm^3/g, respectively. The parameters found are comparable to the charcoals parameters and allowed us to consider the selected material as the basis for obtaining an iodine sorbent.

For the production of test samples, disks with a diameter of 50.0 ± 0.1 mm were cut out of the fabric cloth and aqua solutions of BaI_2 and TEDA were applied using a medical syringe. The auqa phase was applied in an amount not to spread beyond the limits of the prepared disk and impregnate it evenly. After that, the material was placed into a dryer and dried to a constant mass at 60 °C. There is the restriction of the drying temperature due to the intensive evaporation of triethylenediamine from the surface and the high partial pressure of its vapors. Thus, three sample sets containing barium iodide, TEDA and their mixture in equal molar ratio were prepared.

The obtained sorbent samples were covered with 20 nm layer of gold to create a conductive coating and then were examined using Vega3 Tescan scanning electron microscope with a lanthanum hexaboride (LaB_6) cathode in high vacuum mode. Examination was performed using an Everhart-Thornley detector for secondary electrons (SE) at an accelerating voltage of 5 kV.

X-ray diffraction patterns of crystalline compounds used in the study were taken using a D2 PHASER (Bruker) with a copper cathode.

The sorption properties of the obtained impregnated carbon fibers were studied at the D. Mendeleyev University research facility, which we described in detail earlier [5,13]. Laboratory air ingested by a membrane pump passed successively through columns (3, 4) filled with NaA zeolite and VSK-5 charcoal, respectively, to purify the gas stream from water vapor and organic impurities present in the air. Part of the flow controlled by a rotameter was directed to a bubbler-type humidifier, and vapors of I-131-labeled methyliodide were diffused from the evaporator to the second part. Then the two streams were connected before entering the test column, forming a mixture of the required relative humidity. The test column (Fig. 1) with an internal diameter of 50 mm was assembled from separate identical segments made of stainless steel, where prepared samples of sorbents were located, as well as a highly efficient iodine charcoal sorbent VSK-5IK [5], that serves primarily for fixing the slip of radioactive methyliodide. A protective column filled with silica gel containing 8% of silver nitrate was placed at the outlet of the unit to localize the radioiodine in case of an emergency release from the evaporator.

The tests were performed under conditions close to the actual operating conditions of industrial iodine adsorbers: temperature range was about 20–50 °C and the linear velocity of the gas flow was 2.3 cm/s. The supply of air containing labeled methyliodide was periodically stopped and the test column was disassembled to measure the accumulated activity. The activity of carbon fiber materials was measured using a scintillation gamma spectrometer (SPC "Doza", sodium iodide-based detector, counting efficiency 8%) at the energy of 364 keV. To compare the activity of the tested samples and the activity of the slip, VSK-5IK charcoal sorbent was split into a fraction of 200–500 μm, and the segments of the tested column were filled with it to a height not exceeding 0.5 $M = \frac{A_s}{A_r} \cdot m(CH_3I)$, mm. The efficiency of capture (E) of radioactive methyliodide was calculated using the equation:

$$E = \frac{A_s}{A} 100\%, \quad (3)$$

where A_s – the activity of the tested sorbent, cps; A – activity supplied to the system and defined as the sum of activities of the tested sorbent and the slip, pps.

To quantify the radioiodine trapped by sorption materials, several comparison samples were prepared, such as carbon fiber

Fig. 1. The layout of the dismountable test column.

disks of the same shape and size as the test samples containing the given amount of labeled methyliodide. The mass amount of trapped radioiodine was determined by the following ratio:

$$M = \frac{A_s}{A_r} \cdot m(CH_3I), \quad (4)$$

where A_r – the activity of the comparison sample, cps; $m\ (CH_3I)$ – the amount of methyliodide in the comparison sample, mg.

The capacity of the sorbent by radioiodine was calculated by the ratio of its captured mass quantity (M) to the area of the carbon fiber sample. Maximum capacity (C_{max}), equal to the ratio of the mass caught methyliodide to the square of the sorbent was found by processing the obtained experimental data on the accumulation of radioiodine by the layer of impregnated carbon with equation $y = C_{max}(1 - \exp(-kx))$ and determining the its coefficients with least squares method. In this equation, x is the total amount of radioiodine supplied to the system, determined by substituting (eq. (4)) the value of A instead of A_s.

3. Results and discussion

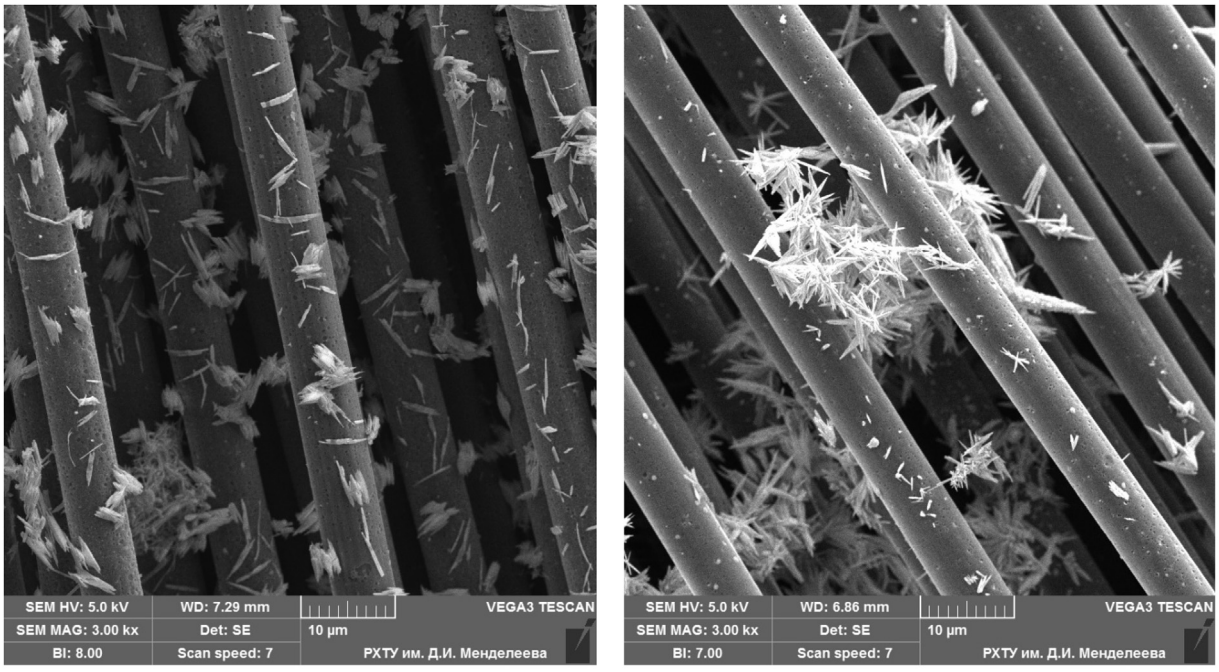
At the initial stage of the study, samples of sorbents containing different amounts of barium iodide were prepared. The mass content of salt (n) was in the range of 1.5–14.0% by weight, that corresponds to 0.04–0.36 mmol/g. The tests were carried out at 30.0 ± 0.1 °C and a relative humidity of the gas stream of 70.0 ± 1.5%. The methyliodide concentration in the gas averaged 85 ± 5 mg/m^3. Table 1 (I) presents comparative sorption characteristics of the obtained samples. The radioiodine trapping efficiency in all cases was calculated by equation (3) after adding about 4 mg of CH_3I to the sorbent.

Evaluating the data obtained, it can be concluded that both the maximum capacity and the radioiodine trapping efficiency by carbon fiber containing barium iodide have the marginal characteristics of 7% salt concentration. In our opinion, this may occur due to a gradual decrease of the specific surface area of barium iodide in the sorbent, caused by the aggregation of salt crystals with increase of its amount in the carbon fiber (Fig. 2). The optimal amount of barium iodide at the rate of 7% by weight fits the literature data [14], where it is indicated that the iodides content in the sorbent in general does not exceed 10% for the effective radioiodine removal.

At the next stage, UVIS® samples containing various amounts of triethylenediamine were prepared. The TEDA mass content (n) in the sorbent was in the range of 0.5–3.0%, which corresponds to 0.04–0.27 mmol/g. Tests were carried out under the same conditions as samples with barium iodide. Table 1 (II) presents comparative sorption characteristics of the obtained materials. The radioiodine trapping efficiency in all cases was calculated by equation (3) after adding about 12 mg of methyliodide to the sorbent. The maximum capacity was found by the same way as for the

Table 1
Methyliodide sorption with UVIS® carbon fiber impregnated with BaI_2 (I) and TEDA (II) at 30 °C and 70% relative humidity.

I	n, %	1.5	3.5	7.0	10.0	14.0
	E, % C, mg/cm^2	85.5 ± 0.8 0.24 ± 0.03	90.4 ± 0.6 0.29 ± 0.03	89.7 ± 0.5 0.56 ± 0.04	86.5 ± 0.7 0.49 ± 0.03	87.7 ± 0.6 0.41 ± 0.03
II	n, %	0.5	1.0	2.0	3.0	
	E, % C, mg/cm^2	87.0 ± 0.7 1.06 ± 0.04	90.1 ± 0.8 1.76 ± 0.05	93.1 ± 0.6 2.83 ± 0.05	97.5 ± 0.7 3.68 ± 0.04	



a b

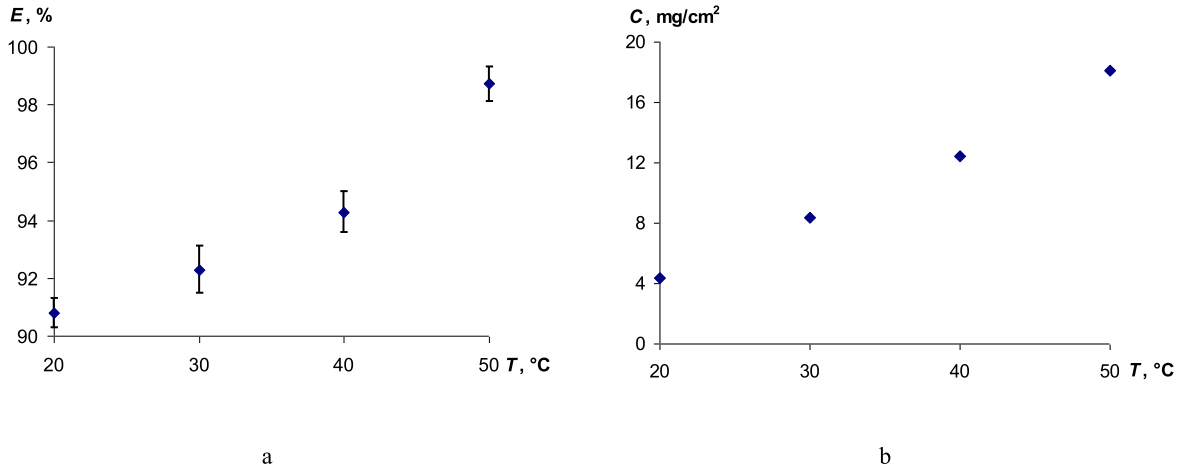
Fig. 2. SEM images of carbon fiber containing 3.0% (a) and 10.0% (b) barium iodide.

sorbents impregnated with barium iodide. The data obtained indicate a significantly higher sorption capacity of samples TEDA containing. At the same time the methyliodide trapping efficiency of these samples is higher even if the exposure time on the laboratory stand is increased three times.

The third stage of the study included sorption tests of UVIS® carbon fiber samples containing the same molar amounts of BaI_2 and TEDA. According to previously obtained data, optimal mass concentrations were selected. They are 7.0% for barium iodide and 2.0% for TEDA, that in both cases is 0.18 mmol/g. Studies were carried out in the temperature range of 25–50 °C at a constant gas flow moisture content of 20.8 ± 0.1 g/m^3 (70% relative humidity at 30 °C) and in the relative humidity range of 20–90% at 30 °C. In all tests the efficiency calculations were performed after adding of about 12 mg of CH_3I to the system. The experimental data obtained indicate an increase of trapping efficiency with the temperature increase (Fig. 3a) from 90.8 ± 0.6% at 20 °C to 98.7 ± 0.7% at 50 °C. The similar dependencies are confirmed by a number of other works [3,14] describing the sorption capacity of iodine sorbents TEDA containing. The rate of chemical interaction (eq. 2) grows with the increase of temperature, but then, when it exceeds 70–80 °C, there is a decrease of efficiency [14], due to the TEDA evaporation from the sorbent surface. The maximum capacity (Fig. 3b) also grows with temperature increase, reaching values of 4.37 ± 0.04 mg/cm^2 at 20 °C and 18.13 ± 0.09 mg/cm^2 at 50 °C.

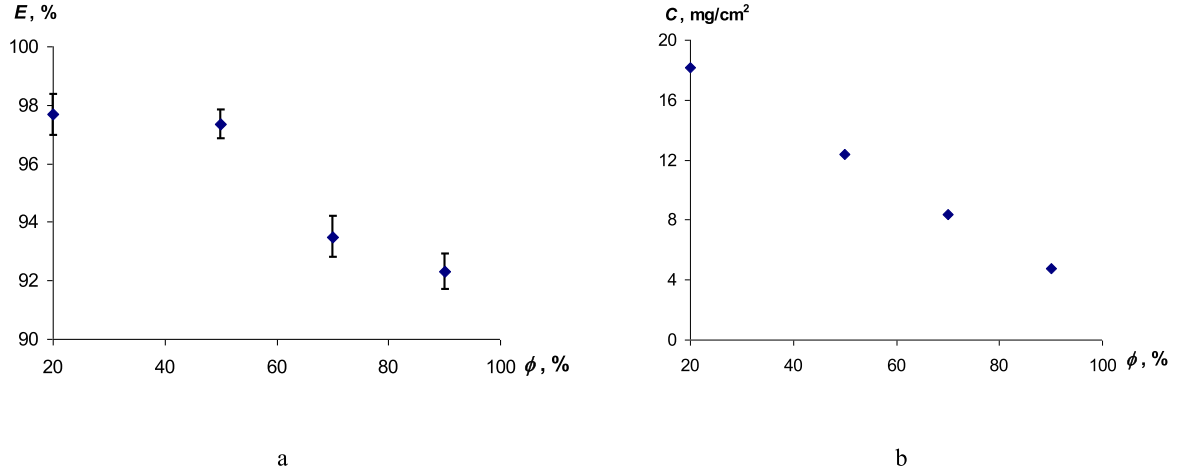
The gas stream humidity also significantly affects both the efficiency (Fig. 4a) and the maximum capacity (Fig. 4b) of the iodine sorbent. Its growth is accompanied by a gradual decrease (97.7 ± 0.6% at 20% humidity and 92.3 ± 0.5% at 90% humidity) of the radioiodine trapping efficiency. This decrease is explained by condensation of water vapor in the sorbent microporous structure [3,15] and subsequent difficulty of methyliodide molecules sorption. However, it is worth noting that even under the most adverse conditions, the capacity value of carbon fiber containing BaI_2 and TEDA does not decrease less than 4.37 ± 0.04 mg/cm^2 and significantly exceeds the capacity of the tested sorbents at the first and second stages of the study.

Comparing the test results, it can be concluded that the trapping efficiency, as well as the radioiodine maximum capacity, in samples containing only barium iodide, is significantly inferior to similar values for samples impregnated with TEDA or a mixture of TEDA and BaI_2 (Fig. 5). In accordance with the IAEA recommendations [16], the nuclear power plant's iodine filter should ensure the methyliodide trapping efficiency from gas streams by at least 99%. Based on the results of the UVIS® samples tests, it can be concluded that 2 layers of material impregnated with 0.018 mmol/g TEDA or



a b

Fig. 3. The trapping efficiency (a) and maximum capacity (b) of iodine sorbents samples on the test temperature.



a b

Fig. 4. The trapping efficiency (a) and maximum capacity (b) of iodine sorbents on the test humidity.

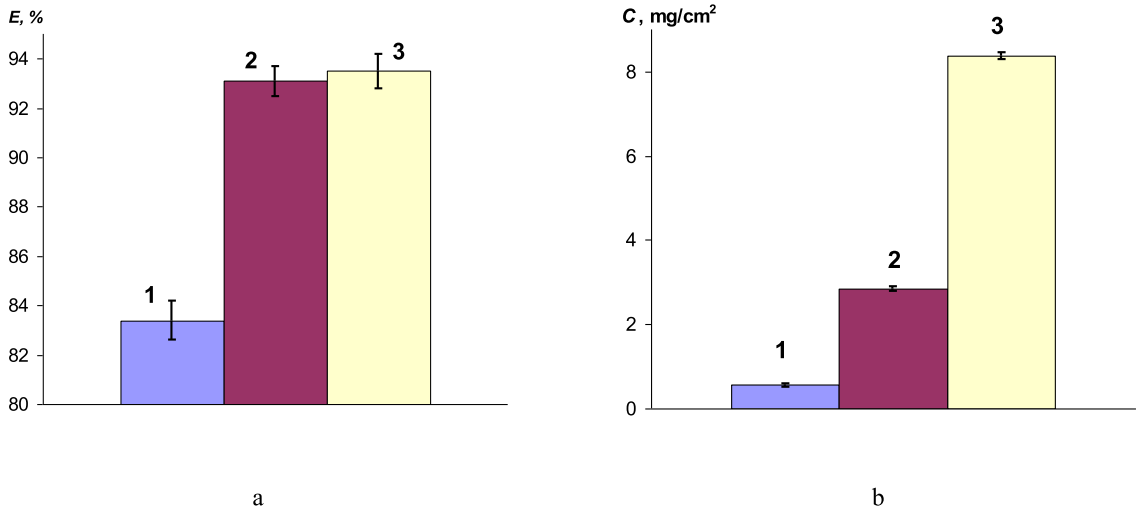


Fig. 5. Comparative sorption characteristics of UVIS® carbon fiber samples impregnated with 0.018 mmol/g BaI_2 (1), TEDA, (2) TEDA and BaI_2 (3); a – the $CH_3^{131}I$ trapping efficiency at 30 °C, 70% humidity and the amount of radioiodine supplied 12 mg; b – the radioiodine maximum capacity at 30 °C and 70% humidity.

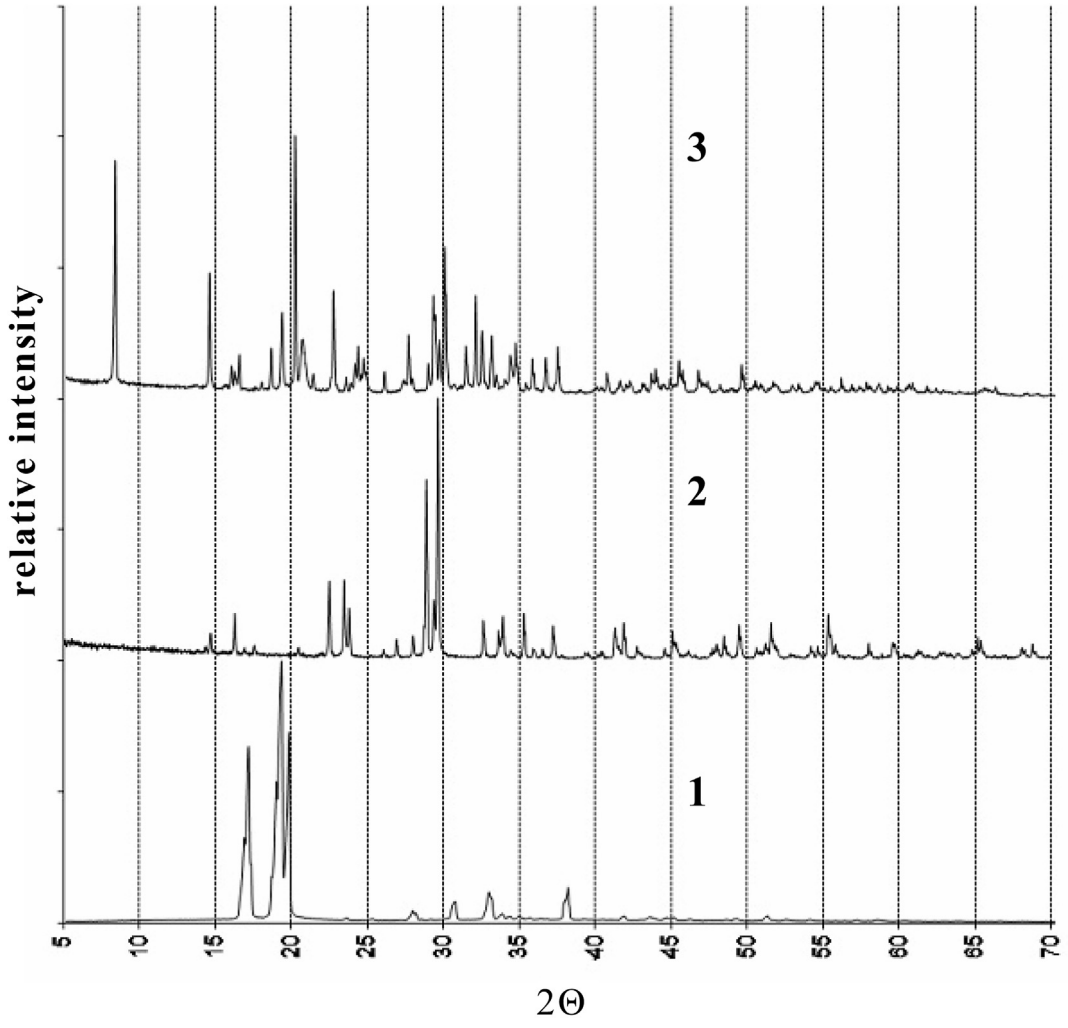


Fig. 6. XRD analysis of crystalline powders 1 - TEDA; 2 - BaI_2; 3 - TEDA and BaI_2 mixture.

TEDA together with BaI_2 will be sufficient to ensure the necessary efficiency. At the same time, at least 3 UVIS® layers containing the same barium iodide molar amount will be required to ensure reliable radioiodine removal from the gas stream.

The resulting data on the maximum capacity of the obtained sorbents are interesting. It is worth noting that the total C_{max} value (Fig. 5b) of samples impregnated with either TEDA or BaI_2 is significantly less than the value of the maximum capacity of a sample impregnated simultaneously with these two compounds. We carried out X-ray phase analysis of TEDA and BaI_2 crystalline powders, as well as their mixtures. The samples for analysis were prepared by evaporation from aqueous solutions. The phase composition of the samples was determined from the diffraction pattern of X-ray radiation on a crystalline powder. The obtained data (Fig. 6) indicate the presence of crystal lattice reflexes in a mixture that differ significantly from the individual compounds reflexes. In other words, the data obtained indicate the new compound formation.

It was not possible to decipher the structure of this compound using the database we possess. However, a search of scientific papers in this area gave some insight into the new compound. In Ref. [17], the authors report on a zeolite-like porous substance obtained as a result of the interaction of TEDA with copper iodide. According to the authors, the structure of this compound is copper iodide, constructed from super-tetrahedral elements $Cu_4I_4(TEDA)_4$. It is noted that its frame is formed by interpenetrating one-dimensional channels along the entire direction. It should be remarked that the conditions for obtaining of this compound differ from the conditions given in our study. However, even its small release will explain the significant capacity increase of the iodine sorbent containing mixture of TEDA and BaI_2. Since the orientation of the methyl groups in the interaction of CH_3I with TEDA is based on nitrogen (eq. 2), the spatial structure of the obtained compound and its porous structure would allow a significantly larger methyliodide amount to interact chemically with the TEDA functional groups.

4. Conclusion

Thus, the results of the studies carried out have shown that UVIS® carbon fiber material can be the basis for the iodine sorbents production used in the NPP premises ventilation system. In our opinion, such sorbents can be effectively used in gas cleaning devices with a roll or zigzag arrangement of the sorption material.

It is shown that the use of barium iodide as an impregnant does not allow achieving sufficiently high efficiency and capacity values for $CH_3^{131}I$ in comparison with the values obtained when testing samples containing the same molar TEDA amount. However, it is worth noting that the final conclusions upon the efficiency of using a particular impregnant in UVIS® carbon fiber material can be made after a number of additional studies. It is important to show the acid gas poisoning effect of this sorbent, the short-term temperature increases effect, and the material aging effect on the radioiodine trapping efficiency from gas flows in our further studies.

A more effective iodine sorbent is carbon fiber containing TEDA and BaI_2. It is shown that both the radioiodine trapping efficiency and the maximum sorbent capacity increase both with an increase of temperature and with a decrease of the gas flow humidity. Having tested the samples impregnated simultaneously with TEDA and barium iodide, it was found that the maximum capacity values of such a sorbent in relation to methyliodide significantly exceed the capacity values of samples containing either TEDA or BaI_2. The explanation to this phenomenon is the formation of a new compound, confirmed by the results of XRD analysis as well as literature data. At the same time, it seems that the compound has a spatial structure that allows methyliodide molecules to penetrate deep into its framework easily and interact with the TEDA functional groups.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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