TRAPPING OF NOBLE RADIOACTIVE GASES AND THEIR DECAY PRODUCTS UNDER STATIC AND DYNAMIC CONDITIONS BY HIGHLY POROUS MATERIALS

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The paper presents the adsorption isotherms for noble gases, in particular, argon, krypton, xenon, calculated assuming static and dynamic conditions based on the VSK-5 charcoal. It proposes methods to describe the obtained dependences that can be further used to calculate Henry's constants. In case of pulse-mode supply of the noble gas under dynamic conditions, relevant calculations are reduced to the Shilov equation that is solved after the adsorptive output curves are fitted. The paper presents the approaches developed to measure the radon trapping efficiency from the air of RW storage facilities.

Keywords: *radioactive waste, radioactive noble gases, sorption, adsorbents, trapping efficiency, adsorption coefficient.*

During the operation of facilities engaged in the management of radioactive substances, special attention should be paid to gaseous radionuclides and their emissions as the least controlled ones. Inert radioactive gases should be singled out as a separate group, which can be conditionally divided into artificial and natural gases.

According to the IAEA recommendation [1], during nuclear power plant operation, radioactive isotopes of inert gases, namely, argon, krypton and xenon should be considered an important factor affecting the environment. Krypton and xenon isotopes result from the fission of nuclear fuel; radioactive isotope ^{41}Ar results from neutron activation of stable isotope ^{40}Ar contained in the air and process flows of nuclear reactors. At the same time, one cannot ignore the fact that if natural sources of ionizing radiation are considered, the main contribution to the exposure dose of the population is made by radon and its decay products [2]. It has been established that it can get accumulated in premises building up to high concentrations: prolonged exposure to it can produce negative impact on human health. Radon isotopes enter the atmosphere from the upper layers of the earth's surface due to the decay of uranium and thorium daughter products available in various rocks of the earth's crust [3], for example, in granites, phosphorites, etc. Radon can be also released into the indoor atmosphere due its exhalation from building materials with high radium concentrations [3].

At nuclear industry enterprises, activated carbons of various grades effectively remove radioactive inert gases from the process flows. According to industry standard existing in Russia [4], sorption capacity of activated carbon with respect to krypton and xenon is calculated under static conditions. For this purpose, the adsorption coefficient

(Henry's constant) is calculated. In this study, argon, krypton and xenon adsorption isotherms were identified at different temperatures using the Quadrasorb automatic analyzer based on activated carbon VSK-5. Adsorption coefficient was calculated at several points of the isotherm using Henry or Langmuir equations. However, the adsorption coefficient calculated according to the Henry model depends significantly on the number of processed points (Figure 1a). The graph presents the mathematical description of the data based on the Langmuir equation, which is considered preferable to describe the initial section of the isotherm.

This may be illustrated by the dependences of the calculated constants plotted on the reciprocal temperature in semi-logarithmic coordinates (Figure 1b). The graphs show that the points calculated based on the Henry model do not lie on a straight line and their values are somewhat underestimated.

Despite the fairly reproducible data obtained under static conditions, it is obvious that under dynamic conditions, especially in the air-carrying gas medium, the Henry constants would differ from the values obtained for adsorption from a pure adsorptive medium, which could further result in incorrect engineering calculations.

To study inert gases adsorption under dynamic conditions, a stand was fitted with its schematic layout shown in Figure 2. The main components of the installation are a thermostated column with a sorbent (1) and an OmniStar Pfieffer Vacuum mass spectrometric gas analyzer (4).

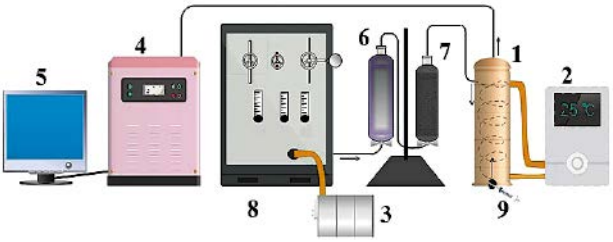

Figure 2. Schematic layout of a stand fitted to study inert gas adsorption under dynamic conditions: 1 – adsorption column; 2 – thermostat; 3 – compressor; 4 – gas analyzer; 5 – personal computer; 6 – column with silica gel; 7 – column with coal; 8 – bench with carrier gas flow regulators; 9 – inlet for inert gases mixture

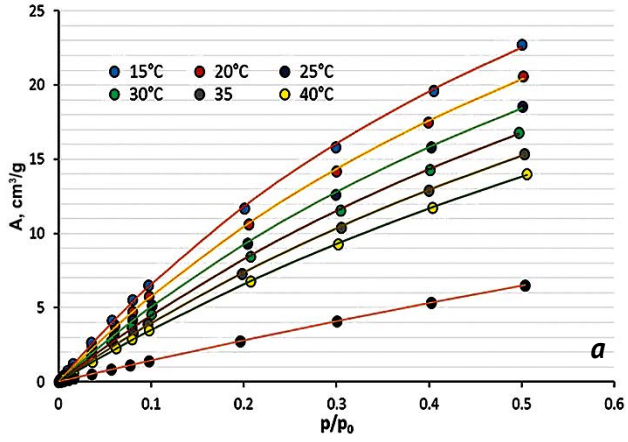

Figure 1. Description of the krypton adsorption isotherms on VSK-5 activated carbon (a); dependence of the Henry's constant logarithm on the reciprocal temperature (b)

The above stand allowed to calculate the output dynamic adsorption curves in the frontal mode as time dependences of relative inert gas concentrations.

In this case, equation (1) was used to calculate the adsorption coefficient for low inert gas concentrations (Henry section) derived from the material balance condition for the adsorption column and taking into account the amount of supplied inert gas minus the amount passed through the column and the amount remaining in all cavities of the adsorption column, including the intergranular space and macropores of the sorbent:

$$K_{\Gamma} = \frac{\rho_{к}}{m} \cdot \left[\upsilon \cdot \left(t_0 - \int_0^{t_0} C_r(t)dt \right) - \left(V_0 + \frac{m}{\rho_{н}} \cdot \varepsilon + V_{п} \cdot m \right) \right], \quad (1)$$

where K_{Γ} is Henry's constant; $\rho_{к}$ is the density of adsorbent particles (apparent density), g/cm³; $\rho_{н}$ is the bulk density of the adsorbent, g/cm³; m is the mass of the adsorbent, g; υ is the volumetric velocity of the gas mixture at the inlet to the coal bed, ml/min; t_0 is the duration of the adsorptive supply, min; V_0 is the free volume of the column, cm; ε is the fraction of free volume in the coal bed; $V_{п}$ is the specific volume of open pores, cm³/g; $C_r(t)$ the adsorbate concentration function at the outlet of the column at time t.

Data on adsorption coefficients can be also obtained from pulsed inert gases mixture supplied to the column (displacement mode). Under this mode,

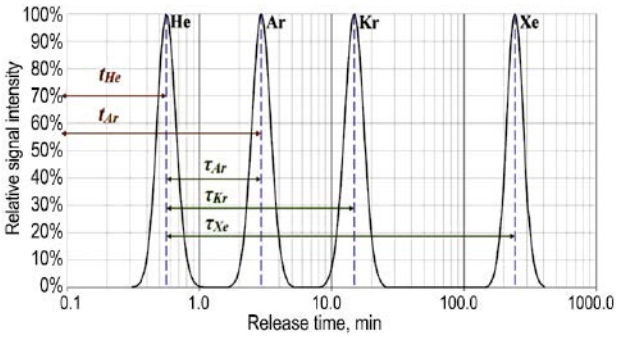

Figure 3. Output curves for inert gases obtained by dynamic adsorption on VSK-5 at 20 °C

output curves can be obtained for several mixture components at once (Figure 3). Given pulsed supply of the inert gas, Henry constant can be calculated based on a basic equation of ideal gas chromatography [5] providing that the Henry constant is directly proportional to the adsorptive retention time and is related to it according to the below equation (2):

$$K_{\Gamma} = \frac{\tau \cdot \upsilon}{m/\rho_{\kappa}} \qquad (2)$$

where τ is the corrected adsorptive release time, which takes into account the correction for the carrier gas velocity through the free volume, and is the difference between the adsorptive release time (peak maximum) and the helium release time.

The results obtained by both methods coincide within the margin of error.

The experimental data obtained show a correlation between the Henry's constant obtained at different temperatures and the boiling point of the adsorptive. Thus, the first way suggests that adsorption coefficients for radon are calculated through the extrapolation of the obtained dependences to the boiling point of radon (Figure 4).

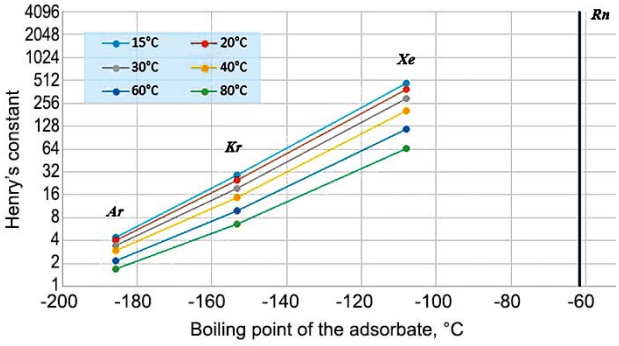

Figure 4. Logarithmic dependence of the Henry constants on the boiling point of the adsorbate

Another option suggests direct experimental study of the sorption capacity for porous materials with respect to radon under dynamic conditions. Such experiments are easily performed using thoron (radon-220), which is a decay product of thorium-228, which is basically explained by the fact that in this case radioactive equilibrium establishes much faster than in the case of radon-222. The second reason is that radiometry is quite handy. Approximately 10—15 minutes after the end of the experiment, the activity of the captured radon-220 is determined by lead-212, which, in turn, has a half-life sufficient for reliable measurement and two characteristic lines of the gamma spectrum 77 and 239 keV. Radiometry was implemented in Multirad Gamma gamma-ray spectrometer given the same geometry. Based on the data obtained, the dependence of the specific activity on the height of the sorption layer was plotted. As can be seen from the graphs (Figure 5), in a fairly wide range of gas supply rates, this dependence appears to be linear. Then, to proceed to the calculation of purification coefficients for another radon isotope (222), one can use the stationary chromatography equation for radioactive gases [6]. In this case, the height of the sorption layer (x) for radon-222 at the required purification factor will be easily calculated from the following ratio:

$$\frac{x_{222}}{x_{220}} \approx \frac{\lambda_{222} \cdot u_{222}}{\lambda_{220} \cdot u_{220}}, \qquad (3)$$

where λ is the decay constant for a given isotope, u is the linear gas flow velocity.

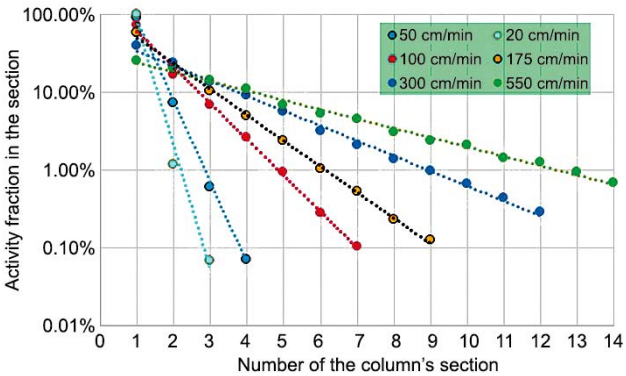

Figure. 5. Distribution of radon-220 activity along the layer of activated carbon VSK-5

Thus, approaches have been proposed to determine the sorption characteristics of various materials with respect to inert gases and radon, in particular. A series of studies is planned to confirm the correlation of adsorption coefficients in the argon-krypton-xenon-radon series for other highly porous materials. Under these studies, the temperature range will be extended to –40 °C. Sorption

properties of such materials as activated carbons, silica gels, zeolites and other materials considered promising in relation to radon will be further studied supporting the selection of most effective and suitable material for gas purification purposes. The approaches developed will eventually help to calculate the required amount of sorbent at the required air exchange rate providing air purification from radioactive isotopes of inert gases, including radon released from the air of RW storage facilities given the available regulatory standards.

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