MEMBRANE METHODS OF SEPARATION OF THE RADIOACTIVE NOBLE GASES. I. EFFECT OF IRRADIATION ON THE PENETRABILITY AND SELECTIVITY OF SEPARATION OF THE NOBLE GASES WITH ASYMMETRIC POLYMER MEMBRANES

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The effect of the radiation load from ^{85}Kr emission is investigated, and also γ-radiation up to a dose of 10^6 Gy on the penetrability of the noble gases and the principal components of air through asymmetric membranes of polyvinyltrimethylsilane (PVTMS) and arylate–siloxane block-copolymer(Silar) in the range of temperatures of the penetrability measurement of 30-90°C. It is established that membranes of PVTMS completely lose mechanical strength at a dose of $1.0 \cdot 10^5$ Gy, but Silar membranes are characterized by constant penetrability, activation energy of penetrability, and selectivity factors of the gases investigated over the whole range of irradiation doses with conservation of mechanism strength. Based on the results obtained, an assumption is made about the feasibility of using asymmetric Silar membranes for the separation of the radioactive noble gases.

In connection with the development of nuclear power generation, problems of protection of the environment from contamination by radioactive noble gases (RNG) are becoming even more urgent. The main consideration is being given to the buildup of short-lived ^{85}Kr, which relates to radionuclides not only of local and regional dispersion, but also of global dispersion.

A review of the methods which are in principal possible for the separation of ^{85}Kr from gaseous effluents is given in [1]. It is shown from analysis that together with the methods of low-temperature adsorption and cryogenic distillation, most developed in technical solution, the separation of ^{85}Kr from waste gases by means of selective polymer membranes is being considered as a promising method. Experience in the use of membrane methods for the separation of stable gases has clearly demonstrated a number of advantages. Here we cite the simplicity of the equipment, the possibility of effecting separation at normal temperatures, safety due to the absence of phase transitions, simplicity of varying the scales of the separation process, its continuous nature, etc.

In order to design a membrane separation system for the RNG, data are necessary on the diffusion parameters of the heavy inert gases in membranes manufactured on a commercial scale, and also information about their stability toward radiation, chemical, temperature, and mechanical effects. It is obvious that recommendations on both the synthesis of gas-separation polymers with specified properties, as well as on the modification of the fabricated materials for the purpose of improving their characteristics, can be obtained only within the framework of detailed investigations of the diffusion properties of polymer substances.

The investigations and development of the membrane method of separation of ^{85}Kr from gaseous effluents, conducted in Japan [2] and the USA [3], are based on membranes of silicone rubber, which is used in the form of films or hollow fibers. Recent achievements in membrane technology are related with the beginning of the commercial manufacture of the so-called asymmetric membranes, which consist of a submicron working layer immediately flush with a porous backing of this same polymer. As a result, a high efficiency of the membrane with quite high separation factors is achieved.

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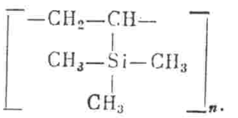
The purpose of the present paper is the study of the possibility of using domestic asymmetric membranes for the separation of ^{85}Kr. The main consideration is given to the determination of the migration parameters of the inert gases and other components of the effluents through polymer materials used in membrane technology, as their comparison will allow mainly the suitability of one or other membrane to be assessed for the solution of the problem formulated. The sensitivity of the membrane to the radiation load from ^{85}Kr emission is a specific but extremely important factor determining the working efficiency of the membrane, and therefore in this report the main attention has been paid to the dependence of the penetrability and selectivity on the radiation dose and also on the temperature.

EXPERIMENTAL

The stable inert gases He, Ar, Kr, Xe, radioactive ^{85}Kr, nitrogen, and oxygen were used in the experiment, i.e., the principal components of gaseous effluents. The penetrability characteristics of asymmetric membranes of polyvinyltrimethylsilane (PVTMS) and arylate—siloxane block-copolymer (Silar) were measured as a function of the radiation load.

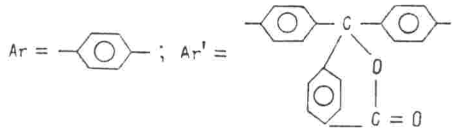
The structure of PVTMS can be expressed by the formula



The molecular mass of the polymer is M = 150,000 and the vitrification temperature T_V = +180°C. The total membrane thickness amounted to 150 μ.

Silar is the block-copolymer of arylate and dimethylsiloxane:

$$\left[-\underset{\underset{O}{\|}}{C}-Ar-\underset{\underset{O}{\|}}{C}-Ar'-O-\right]_x-[Si(CH_3)_2-O]_y-, \text{ where}$$



T_V of arylate and dimethylsiloxane amounts to —110°C and +280°C respectively. Silar of composition 46/54 was used in the experiment, which corresponded to x/y = 10/70. The Silar membranes had a working layer thickness of 2-3 μ.

Irradiation of the membranes was carried out by two methods: by the γ-emission of a ^{60}Co source on the RKhM-γ-20 facility in an atmosphere of air at room temperature (dose intensity 50 Gy/sec, doses: 2, 4, 6, and $10 \cdot 10^5$ Gy) and by direct holding at normal pressure in an air atmosphere with a ^{85}Kr content of $7.4 \cdot 10^{11}$ Bq (dose intensity 0.02 Gy/sec, dose $1.4 \cdot 10^5$ Gy). Dosimetry was carried out by infrared spectroscopy of polyethylene films irradiated together with the membrane samples [4], with an accuracy of the dose determination of ±10%.

The determination of the migration parameters of the gases through the membranes were carried out by the penetrability method on facilities with detectors of the radiometric [5] (in the case of krypton and labeled ^{85}Kb) or chromatographic [6] type. In the latter case the experiment was conducted in the following way: The membrane being investigated was mounted hermetically in a closed chamber and the diffusion cell was divided into two parts — reservoir and collector. The volume of the reservoir and collector was equal to 0.5 cm^3 and the working surface of the membrane was 15 cm^2. At a defined instant, the gas being investigated was started into the reservoir and its migration kinetics into the receiver — which was continuously purged with helium as a gas-carrier — were studied (when determining the penetrability of He and H_2, argon was used as the carrier gas). The carrier gas carried away the substance which had diffused into the analyzing system of an LKhM-8MD gas chromatograph with a katharometer as the detector. In the course of the experiment, the dependence of the gas flow through the membrane on the time was recorded. After reaching a steady diffusion state, a sample of the diffused gas was withdrawn by means of a stopcock-batcher and the content of the diffusant in it was analyzed.

TABLE 1. Penetrability Q_∞ of Asymmetric Membranes of Silar 46/54 at 25°C versus Irradiation Dose

Dose, Gy·10^5	Type of irradiation	$Q_\infty \cdot 10^8$, mole/m²·sec·Pa					
		He	Ar	Kr	Xe	O_2	N_2
0		2.4	2.8	4.8	8.4	3.0	1.6
2	γ	2.4	2.8	4.8	8.6	3.0	1.5
4	γ	2.4	2.9	4.7	8.2	2.9	1.5
6	γ	1.6	1.9	3.1	5.6	1.9	1.0
10	γ	1.9	2.2	3.5	5.5	2.4	1.2
1.4	Exposure in the atmosphere with ^{85}Kr	2.7	3.1	5.0	8.2	3.2	1.7

TABLE 2. Selectivity Factors α of Asymmetric Membranes of Silar 46/54 at 25°C versus Irradiation Dose

Dose, Gy·10^5	Type of irradiation	α					
		Kr/N_2	Kr/O_2	Xe/N_2	Xe/O_2	Xe/Kr	O_2/N_2
0		3.1	1.6	5.3	2.7	1.7	1.9
2	γ	3.1	1.6	5.6	2.9	1.8	2.0
4	γ	3.1	1.6	5.5	2.9	1.9	1.9
6	γ	3.1	1.6	5.5	2.9	1.8	1.9
10	γ	3.0	1.5	4.7	2.3	1.6	2.0
1.4	Exposure in the atmosphere with ^{85}Kr	3.0	1.6	4.9	2.6	1.6	1.9

TABLE 3. Activation Energy of Penetrability E_{Q_∞} of Irradiated Asymmetric Membranes of Silar 46/54

Dose, Gy·10^5	Type of irradiation	E_{Q_∞}, kJ/mole					
		He	Ar	Kr	Xe	O_2	N_2
0		74	50	36	24	48	64
2	γ	69	48	31	24	45	62
4	γ	79	52	36	17	52	67
6	γ	76	52	36	26	52	67
10	γ	81	48	36	22	55	69
1.4	Exposure in the atmosphere with ^{85}Kr	72	50	36	22	52	64

Experiments were conducted at four temperatures: 30, 60, 80, and 90°C, and the accuracy of the thermostatic control was ±0.5°C. Two membranes were used with a single radiation dose and four parallel measurements were carried out at each temperature.

The principal characteristic of the gas-separation membrane is the penetrability constant of the gases P, which is calculated by the formula [7]

$$P = \frac{C_i \cdot V \cdot H}{100 \cdot S \cdot \Delta p}, \quad \frac{\text{mole} \cdot \text{m}}{\text{m}^2 \cdot \text{sec} \cdot \text{Pa}} \tag{1}$$

where C_i is the concentration of gas having passed through the membrane into the collector, vol. %; V is the carrier gas flow into the collector, mole/sec; H is the thickness of the membrane, m; S is the area of the membrane, m²; and Δp is the partial pressure of the gas being investigated in the reservoir, Pa.

In formula (1), the thickness of the working layer H occurs as a parameter — a quantity, strictly speaking, which is unknown for the case of asymmetric membranes, and therefore we have confined ourselves to the calculation of the penetrability Q_∞ — the steady state flow through the membrane:

$$Q_\infty = \frac{C_i \cdot V}{100 \cdot S \cdot \Delta p}, \quad \frac{\text{mole}}{\text{m}^2 \cdot \text{sec} \cdot \text{Pa}} \tag{2}$$

The quantity Q was determined with an accuracy of ±10%.

Knowledge of the penetrabilities is sufficient for calculating the selectivity factors α of different gas vapors:

$$\alpha_{ij} = \frac{Q_{\infty i}}{Q_{\infty j}} = \frac{P_i}{P_j}. \quad (3)$$

RESULTS AND DISCUSSION

The first tests on the radiation stability of the membranes investigated revealed that PVTMS completely loses mechanical strength at radiation doses in excess of $1 \cdot 10^5$ Gy, and therefore subsequent determinations to determine the dependence of the penetrability on the radiation dose were carried out on Silar membranes.

Table 1 shows the results of the determination of the penetrability of inert gases and components of air through asymmetric membranes of Silar 46/54, irradiated with doses right up to $10 \cdot 10^5$ Gy. The statistical analysis of the data carried out shows that membranes of Silar have almost unchanged parameters of gas-permeability up to doses of $10 \cdot 10^5$ Gy. The mechanical properties in this case remain unchanged. Irradiation has no effect on the selectivity factor in the whole range of doses investigated (Table 2).

The temperature dependence of the penetrability of irradiated Silar membranes is described well by Arrhenius's law. The calculated activation energies of penetrability are given in Table 3, from which it can be seen that an irradiation dose up to $10 \cdot 10^5$ Gy has no effect on the activation energy of penetrability of the gases investigated.

The results obtained on the radiation strength of polymer membranes of different type confirm the well-known rule of radiation chemistry: Linear polymers under the action of radiation are cross-linked and their mechanical properties are even improved somewhat (the melting point etc. is increased), but branched polymers are destroyed. In the course of destruction of vitreous PVTMS, a considerable quantity of gases is liberated and the polymer disintegrates. The diffusion and mechanical characteristics of Silar are almost independent of the irradiation dose. Silar remains stable up to at least a dose of $10 \cdot 10^5$ Gy. With increase of the absorbed dose, the penetrability is reduced slightly, as the cross-linking of the polymer chains makes difficult the migration process. However, as the diffusion is determined by the fluctuations of certain links of the polymer chain, and not by the whole molecule, then for a significant effect on diffusion it is necessary that the number of links should attain 100-200 per polymer molecule, which certainly has not been observed with the irradiation doses used. The selectivity is almost indepndent of the absorbed dose, although some increase would be expected in view of the well-known relationship: The lower the diffusion coefficient, the higher is the selectivity. Essentially, the results obtained confirm the recommendations [8] for the use of membranes of silicone rubber for the separation of ^{85}Kr right up to doses of $10 \cdot 10^5$ Gy (these membranes lose working efficiency at doses of around $15 \cdot 10^5$ Gy).

The result on the conservation of the working efficiency of Silar membranes when irradiated directly with the radiation from ^{85}Kr located both outside and inside the membrane is interesting. In the experiments conducted up to now (see, for example [9]), the radiation from krypton was simulated with external irradiation, namely, γ-rays from ^{60}Co. The present investigation directly confirms the adequacy of this simulation, at least at the level of doses up to $1.4 \cdot 10^5$ Gy.

The values of the penetrability of the gases investigated reflect the competitive ability for the use of Silar membranes by comparison with silicone rubber membranes for the separation of ^{85}Kr. Actually, the separation factor of Kr/N_2 for silicone rubber is equal to 3.5 [10], and the present paper gave a value of 3.1. The slight reduction of the separation factor for Silar in no way reduces its possibilities, as in contrast from silicone rubber, Silar allows asymmetric membranes of very high penetrability to be obtained which, in their turn, allows the area of the membrane used for the treatment of this gas flow to be reduced. It can be hoped that radiation-stable asymmetric membranes of Silar will find application as the principal element of cascade systems for the purification of gaseous effluents from the radioactive noble gases.

In conclusion, we note that because of the low radiation stability, PVTMS membranes can be used in cascade stages with a low radiation loading, and also for the separation of mixtures of xenon and krypton, and the separation of pure xenon for the purpose of its utilization. In the latter case, as membranes of PVMTS possess an "inverse" selectivity nature with respect to xenon and krypton ($\alpha_{Xe/Kr}$ of Silar = 1.7, and $\alpha_{Xe/Kr}$ of PVMTS = 0.45), they are placed advantageously in modules, including membranes of different types of selectivity, for example, in combination with Silar membranes. It is obvious that such modules will be characterized with significantly higher separation parameters than the normal membranes [11].

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MEMBRANE METHODS OF SEPARATION OF THE RADIOACTIVE NOBLE GASES. II. INVESTIGATION OF DIFFUSION AND PERMEABILITY OF INERT GASES AND AIR COMPONENTS THROUGH FILMS BASED ON POLYDIMETHYLSILOXANE

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The transport characteristics of the inert gases, N_2, O_2, CH_4, CO_2, and H_2 as the main components of gaseous discharges have been measured by the differential permeability method at various temperatures, in homogeneous films of arylate–siloxane block copolymer (Silar) of various composition and also in its components viz. polydimethylsiloxane (PDMS) and polyarylate. The dependence of the diffusion and permeability coefficients on the inert gas atomic dimensions, and of the solubility coefficients on the force constants for the Lennard-Jones potential, were analyzed. It was shown that the selectivity of gas permeability of Silar was determined by the properties of the siloxane component and the sizes of the permeability coefficients were reduced with an increase in the proportion of polyarylate block due to the predominant reduction in diffusion coefficients in comparison with the solubility coefficients.

Preliminary investigations on the influence of irradiation on the permeability and selectivity of polymeric asymmetric membranes in relation to components of gaseous discharges [1] showed that membranes of Silar material superseded membranes of silicone rubber in their radiation stability. Silicone rubber membranes are acknowledged to be the best polymeric material for the purification of gaseous discharges of radioactive noble gases (RNG) [2]. It therefore seemed necessary to study in more detail the transport characteristics of this

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