

The efficiency of the sorbent was estimated by the value of sorption S , % and distribution coefficient K_d , ml/g of each radionuclide, which were calculated according to the following equations:

$$S = \frac{A_0 - A}{A_0} \cdot 100, \quad (1)$$

$$K_d = \frac{A_0 - A}{A} \cdot \frac{V}{m}, \quad (2)$$

where A_0 – initial activity of radionuclide in solution before sorption, Bq; A – equilibrium activity of radionuclide in solution after sorption, Bq; V – volume of solution, ml; m – mass of sorbent, g.

Results and Discussion. Figures 1–6 (left) show the isotherms of low-temperature nitrogen adsorption-desorption on investigated oil shale samples. All isotherms are irreversible and have hysteresis loops. This fact indicates the presence of mesopores (2–50 nm) in the samples [13], in which, along with multilayer adsorption, capillary condensation of nitrogen occurs [14]. The isothermal curves of nitrogen adsorption-desorption by oil shale belong to Type IV according to the IUPAC classification [13]. The shape of the hysteresis loop is close to the Type H3, which is inherent to sorbents having disordered, lamellar pore structure, slit- and wedge-shaped pores [15]. The gentle slope of the adsorption curve within the p/p_0 range of ~ 0.05 – 0.30 indicates an appreciable overlap of monolayer and multilayer adsorption, when the precise interpretation of the specific monolayer capacity is questionable [13].

It should be noted that neither the heating rate of oil shale, nor their steam treatment affect the shape of low-temperature nitrogen adsorption-desorption isotherms.

Fig. 1–6 (right) show pore size distribution (PSD-plots) for all the samples of modified oil shale studied in the current work.

Fig. 1. Isotherm of low-temperature nitrogen adsorption-desorption (left) and PSD-plots (right) for a sample of oil shale heated at a rate of 2 deg/min at the first stage without subsequent steam treatment at the second stage

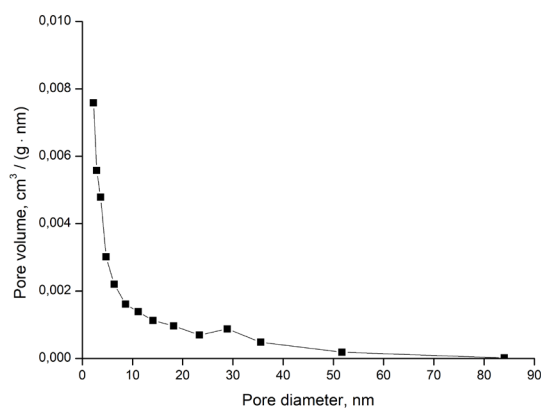


Fig. 2. Isotherm of low-temperature nitrogen adsorption-desorption (left) and PSD-plots (right) for a sample of oil shale heated at a rate of 5 deg/min at the first stage without subsequent steam treatment at the second stage

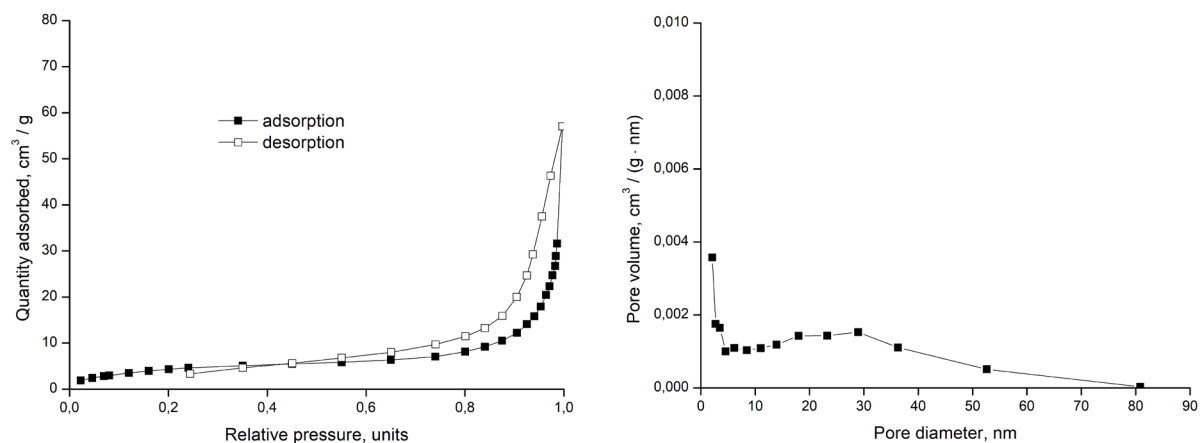


Fig. 3. Isotherm of low-temperature nitrogen adsorption-desorption (left) and PSD-plots (right) for a sample of oil shale heated at a rate of 10 deg/min at the first stage without subsequent steam treatment at the second stage

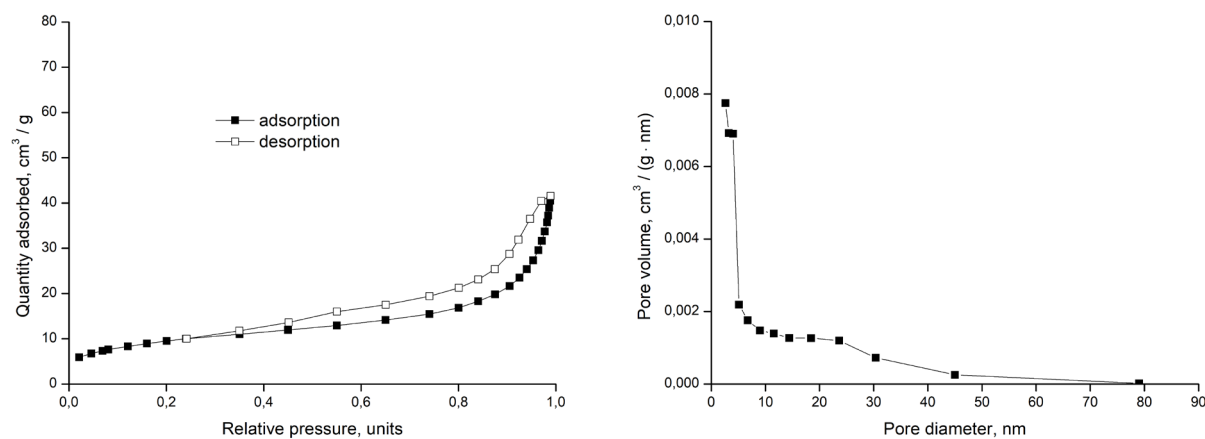


Fig. 4. Isotherm of low-temperature nitrogen adsorption-desorption (left) and PS-plots D (right) for a sample of oil shale heated at a rate of 2 deg/min at the first stage with the subsequent steam treatment at the second stage

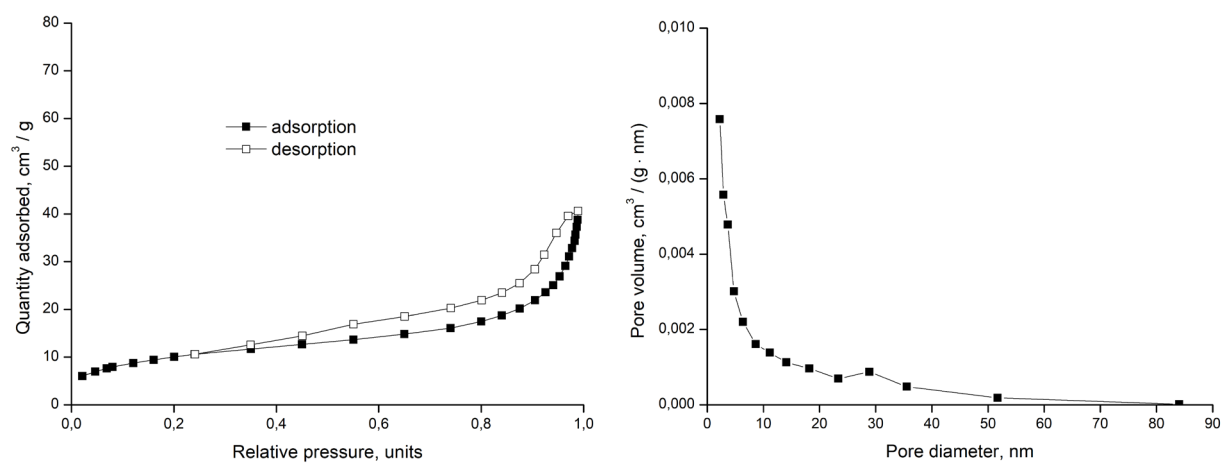


Fig. 5. Isotherm of low-temperature nitrogen adsorption-desorption (left) and PSD-plots (right) for a sample of oil shale heated at a rate of 5 deg/min at the first stage with the subsequent steam treatment at the second stage

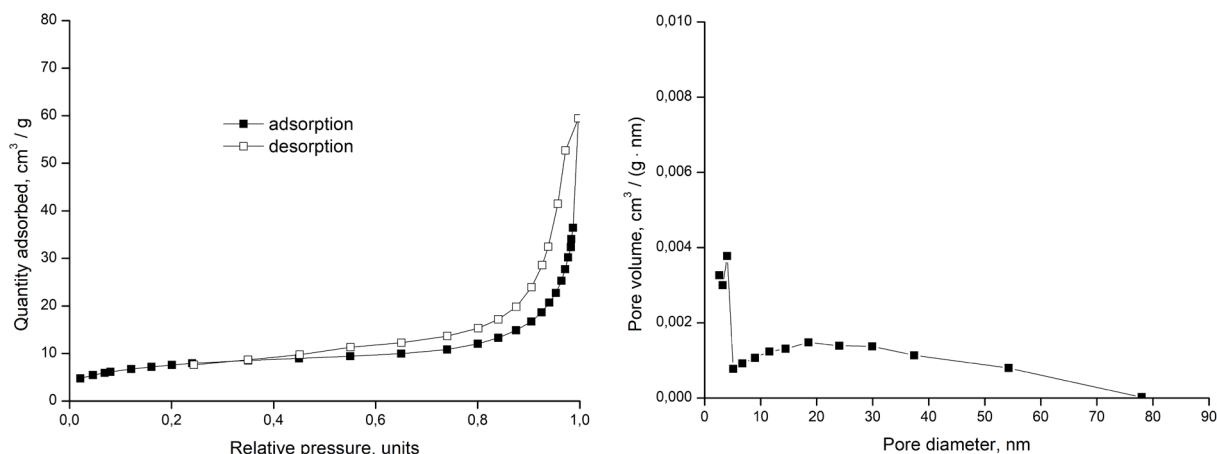


Fig. 6. Isotherm of low-temperature nitrogen adsorption-desorption (left) and PSD-plots (right) for a sample of oil shale heated at a rate of 10 deg/min at the first stage with the subsequent steam treatment at the second stage

Fig. 1–6 show that most of the pores of modified oil shale have sizes corresponding to mesopores. The treatment of sorbents with steam does not significantly affect the shape of the PSD-curves, although it does affect the total pore volume and, consequently, the intensity of the mentioned curves.

It should also be noted that heating the oil shale at a rate of 10 deg/min leads to a decrease in the total pore volume in comparison with the samples heated at rates of 2 and 5 deg/min. Such changes are probably associated with the partial destruction of oil shale particles at a higher heating rate. In addition, for samples with a heating rate of 10 deg/s, there is an increase in the number of pores with an average pore size of 20–30 nm comparing with pores of other size, which is due to the more intense carbonization of the organic component of the oil shale and its removal from the pores.

The values of the surface area and pore parameters of modified oil shale sorbents before and after steam treatment are presented in Table 1. The data are obtained on the basis of experiments on low temperature nitrogen adsorption-desorption by modified oil shale samples.

Table 1. Values of specific surface area and pore parameters of the modified oil shale samples

Heating rate, deg/min	Specific surface area, m²/g				Pore volume, cm³/g				Average pore size, nm			
	without steam treatment		steam treatment		without steam treatment		steam treatment		without steam treatment		steam treatment	
	A_{sp}	A_{BET}	A_{sp}	A_{BET}	$V_{sp,ads}$	$V_{sp,des}$	$V_{sp,ads}$	$V_{sp,des}$	D_{ads}	D_{des}	D_{ads}	D_{des}
2	15	18	33	35	0.053	0.048	0.058	0.063	14	13	7	8
5	15	18	35	37	0.049	0.059	0.055	0.061	13	16	6	7
10	15	17	26	28	0.045	0.072	0.053	0.082	12	19	8	12

The largest specific surface area corresponds to sorbents which are heated at a rate of 2 (33–35 m²/g) and 5 deg/min with the subsequent steaming (35–37 m²/g). For the other studied samples, the specific surface area is about 15–28 m²/g. The specific surface area increases by ~ 2 after steam treatment.

The real volume and average pore size of the sorbents, due to the presence of hysteresis on the nitrogen adsorption-desorption isotherms, is recommended to be estimated by the values obtained from desorption curve. The reason is that desorption conditions (due to the lower pressure of the saturated vapor above the meniscus of the liquid in the pore) are closer to equilibrium than adsorption conditions [16]. Among samples without steaming, the largest pore volume corresponds to the samples which are heated at a rate of 5 and 10 deg/min (0.059 and 0.072 cm³/g respectively). Among the oil shale treated with live steam, a sample with a heating rate of 10 deg/min at the first stage has the largest pore volume (0.082 cm³/g). It can be seen that higher heating rate of oil shale, as well as its treatment with live steam, increases the total pore volume of the sorbent.

According to Table 1, the steam treatment of oil shale leads to a decrease in pore diameter of the sorbent by a factor of ~ 2 . This is due to appearance of a large number of new small pores, which is associated with the removal of shale organic component. Presumably, the size and shape of existing pores increases in length, although the pores' diameter does not change. This assumption also explains the increase in total pore volume of oil shale after steam treatment. The heating rate of oil shale at the first stage affects the average pore diameter insignificantly, although when the oil shale is heated at a rate of 10 deg/min, there is a slight increase in the average pore size, the reason for which is explained above.

The general regularities of the influence of different processing regimes on the parameters of pores and surface area of oil shale are as follows: steam treatment increases the surface area of the samples, reduces the average pore size and increases the total pore volume significantly. At the same time, the heating rate of oil shale at the first stage of treatment has an insignificant effect on the values of pore size and surface area. The values of sorption and distribution coefficient for each radionuclide by all the studied samples of oil shale are presented in Table 2.

Table 2. Sorption and distribution coefficients of cesium, strontium and cobalt radionuclides on the samples of modified oil shale

Heating rate, deg/min	^{137}Cs				^{85}Sr				^{60}Co			
	without steam treatment		steam treatment		without steam treatment		steam treatment		without steam treatment		steam treatment	
	$S, \%$	$K_d \cdot 10^{-3}, \text{ml/g}$	$S, \%$	$K_d \cdot 10^{-3}, \text{ml/g}$	$S, \%$	$K_d \cdot 10^{-3}, \text{ml/g}$	$S, \%$	$K_d \cdot 10^{-3}, \text{ml/g}$	$S, \%$	$K_d \cdot 10^{-3}, \text{ml/g}$	$S, \%$	$K_d \cdot 10^{-3}, \text{ml/g}$
2	76 $\pm$ 2	3.2 $\pm$ 0.3	82 $\pm$ 1	4.7 $\pm$ 0.4	69 $\pm$ 1	2.8 $\pm$ 0.2	79 $\pm$ 1	3.7 $\pm$ 0.2	73 $\pm$ 2	3.7 $\pm$ 0.5	88 $\pm$ 1	7.2 $\pm$ 0.8
5	91 $\pm$ 1	10.4 $\pm$ 0.5	82 $\pm$ 1	4.5 $\pm$ 0.2	72 $\pm$ 1	2.6 $\pm$ 0.1	75 $\pm$ 1	3.0 $\pm$ 0.1	94 $\pm$ 1	15.6 $\pm$ 3.4	94 $\pm$ 2	16.6 $\pm$ 4.8
10	81 $\pm$ 1	4.5 $\pm$ 0.3	80 $\pm$ 1	4.2 $\pm$ 0.3	66 $\pm$ 1	2.0 $\pm$ 0.1	69 $\pm$ 1	2.4 $\pm$ 0.1	74 $\pm$ 1	3.0 $\pm$ 0.3	81 $\pm$ 2	4.3 $\pm$ 0.4

All the sorbent samples studied in this work show high efficiency in sorption of ^{137}Cs , ^{85}Sr , and ^{60}Co from solutions simulating LRW: the values of sorption and distribution coefficient were 76–91 % and $(3.2\text{--}10.4) \cdot 10^3 \text{ ml/g}$, 66–75 % and $(2.0\text{--}3.7) \cdot 10^3 \text{ ml/g}$, 73–94 % and $(3.0\text{--}16.6) \cdot 10^3 \text{ ml/g}$, respectively.

The most effective sorbent for complex purification of model LRW solution via sorption is modified oil shale obtained by heating rate of 5°C/min at the first stage and without steam treatment at the second stage. The values of the distribution coefficient for ^{137}Cs , ^{85}Sr , and ^{60}Co were $4.4 \cdot 10^3$, $3.0 \cdot 10^3$, $16.6 \cdot 10^3 \text{ ml/g}$ for this sorbent, respectively.

Although the increase is insignificant, it should be noted that, in general, the steam treatment of oil shale increases the efficiency of sorption of radionuclides on sorbents. Among all the samples of oil shale sorbents, the greatest increase in efficiency of radionuclide sorption is noticed for the sample with a heating rate of 2 deg/min. After the live steam treatment, the distribution coefficients of radionuclides on the sorbent increase as follows: by 1.5 times (from $3.2 \cdot 10^3$ to $4.7 \cdot 10^3 \text{ ml/g}$) for ^{137}Cs , by 1.7 times (from $2.2 \cdot 10^3$ to $3.7 \cdot 10^3 \text{ ml/g}$) for ^{85}Sr and by 2.7 times (from $2.6 \cdot 10^3$ to $7.1 \cdot 10^3 \text{ ml/g}$) for ^{60}Co .

Obviously, an increase in the efficiency of sorption of radionuclides on steam-treated oil shale occurs due to an increase of the available surface area of the sorbent, as well as an increase of the total pore volume.

Conclusions. Modified oil shale is a promising sorbent for treatment of LRW containing ^{137}Cs , ^{85}Sr , and ^{60}Co . The distribution coefficients of these radionuclides on the indicated sorbents are $\sim 10^3\text{--}10^4 \text{ ml/g}$ and sorption values are above 66 %. Due to its low cost, chemical, thermal and radiation resistance, low rate of leaching of radionuclides from contaminated sorbents, as well as the possibility of disposal spent sorbents with minimal conditioning, oil shale is a very attractive material for LRW treatment.

Undoubtedly, understanding and testing the effects of the pore system contributes to a better control of the adsorption activity of complex systems, so that radionuclide adsorbents with improved designs could become accessible. The live steam treatment of oil shale increases its efficiency as a sorbent only slightly. To obtain the most effective sorbents for the sorption of ^{137}Cs , ^{85}Sr , and ^{60}Co from LRW, it is recommended to process oil shale with the method indicated in the work at a heating rate of 5 deg/min without or with subsequent steam treatment. Steaming intensifies the removal of the organic component of oil shale, which leads to the increase of available surface area of the sorbent, as well as total volume of its pores.

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