# Radioactive Pollution of Soils of Kola Peninsula and Their Deactivation

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# **Abstract**

Processes of sorption and desorption of cesium and strontium radionuclides by main rock-forming minerals and soil samples from Kola PEN have been studied. It has been demonstrated that it is advisable that acidified solution of sodium chloride should be used to desorb radionuclides. A promising flow diagram has been proposed for deactivation of soils that have been polluted by radionuclides. The flow diagram involves a high degree of concentrating the radionuclides within a product to be buried, the use of a recycled solution that is intended for soil deactivation, as well as the freedom from the secondary pollution of soil by reagents harmful for the environment.

## INTRODUCTION

Soils from some territories of Russia, as well as from CIS states (Ukraine, Belarus) are polluted by radionuclides and they need rehabilitation. Cesium and strontium radionuclides, the characteristics of which are presented in Table 1, rank among the major fission products, the constituents of the radioactive wastes [1].

The soil that is polluted by radionuclides is suggested to be taken out to store at special ranges [2]. However, its volumes, as a rule, are great, and it is impossible to provide the long-term safe storage of this soil in view of large expenses. Thus, it is more advisable to conduct deactivation of soil *in situ* by its treatment with solutions of reagents and by sorption extraction of the radionuclides that have passed into solution.

When choosing the reagents for desorption, issues of processing of the received solutions and the secondary pollution of subsoil waters by the residues of the reagents that have been used for the deactivation typically were not considered [3–7]. The proposed employment of solutions of ammoniac and nitrate compounds for the deactivation is attended with the emergence of hard-to-remove problems, since compounds

of nitrogen that remain in soil may enter subsoil waters and water basins, where their MPC are rigidly limited. Deactivation methods for the formed radioactive solutions and for the subsequent salvaging of the deactivated solutions have not been developed [3–8].

In addition, desorption was typically investigated without taking into account the composition of minerals and organic matter that form soil; however, this limits the possible use of the acquired data for a prospective estimation of the efficiency of soil desorption for various regions.

This work explores the processes of the suggested new technology to deactivate soils by the example of the main rock-forming minerals and soil samples from Kola PEN. Sorption of cesium and strontium radionuclides by soil components, as well as their desorption by chloride

TABLE 1 Characteristics of cesium and strontium radionuclides, the constituents of radioactive wastes

Radio-	Half-life	$E_{\rm max}$ , MeV	
nuclide	period	$\beta$ -radiation	γ-radiation
<sup>137</sup> Cs	30 years	1.20	0.66
<sup>90</sup> Sr	28.5 years	0.61	_

solutions from particular constituents of soils have been investigated. When choosing chloride solutions for the desorption, we made allowance for possible selective sorption of cesium and strontium radionuclides from chloride solutions of complex composition [9, 10], as well as considerably higher MPC of chloride ion as compared to  $\mathrm{NO}_3^-$  and  $\mathrm{NH}_4^+$  ions also in water basins of various purpose, where subsoil waters may fall. This makes it possible to minimize the risk that is related to the secondary pollution of water.

## **EXPERIMENTAL**

Sorption and desorption were investigated by chemical and radiometric methods. When studying sorption by a chemical method, 2.5 g of a soil sample was put in 100 ml of a solution that contained 7 10<sup>-4</sup> mol/l of cesium or strontium chlorides. Desorption was conducted with chloride solutions of a selected composition for 1 h under static conditions under stirring of the suspension. After a certain time, a solid phase was separated from the solution. The solution was analysed for cesium or strontium content by methods of flame photometry and atomic emission spectrometry with induction-linked plasma.

Nitrates of <sup>134</sup>Cs and <sup>90</sup>Sr radionuclides were used as indicators in the radiometric research. A specific radioactivity was measured by radiometric methods in integral and differential regimes with certificated instrumentation: UMF-1500 D low-background unit, and PSO2-08 and DRG-01 T radiometers. Exposition time comprised up to 1800 s depending on the activity of metering samples and on their masses. The error of radionuclide determination for the confidence probability that was equal to 0.95 averaged 11 %. To measure the activity of the preparations, Teflon, polyethylene, or metal 1–2 ml targets of a conic or cylindrical form were used.

Mineral samples, 0.5 g in mass, in glass weighing bottles were covered with 20 ml of solutions with tracer<sup>134</sup>Cs or <sup>90</sup>Sr, activity of which comprised  $1.44\ 10^3$  and  $0.21\ 10^3$  kBq/kg at the respective concentrations  $5.8\ 10^{-10}$  and  $9.4\ 10^{-10}$  mol/l. Sorption processes were also investigated in static conditions. After certain time

periods, 1 ml of the liquid phase was taken out to carry out  $\gamma$ - and  $\beta$ -measurements. After gauging, the solutions returned in the process. The quantity of a sorbed isotope was determined from a difference of the activity of the initial solution and a solution upon contacting to a mineral.

To research desorption, a solid phase was initially saturated with radionuclide, separated from the solution, and with no washing, it was put into a deactivating solution. Cesium or strontium passing from a mineral into solution was controlled from the activity of the liquid phase. After certain time terms, 1 ml of the liquid phase was taken out to carry out  $\gamma$  and β-measurements. After gauging, the solutions returned in the process. The desorption degree was determined from the ratio of the activity that has passed into the liquid phase to the initial activity. Upon the equilibrium was reached, the phases were separated, dried,  $\gamma$ - and  $\beta$ -activities were measured, and their balance was calculated. In the sorptiondesorption experiments, the ratio  $\alpha$  of the volume of a liquid phase (L) to the mass of a solid phase (S) was equal to 40.

The concentrates that were received by enriching procedures and that contained at least 92-95 % of the main mineral and the components, similar in their physicochemical properties, as the main impurities were used for the investigations. During the course of enriching, minerals were not subjected to chemical treatment, lest their sorption properties be modified. The main minerals of granite rocks: phlogopite KMg<sub>3</sub>(AlSi<sub>3</sub>O<sub>10</sub>)(OH)<sub>2</sub> and muscovite KAl<sub>2</sub>(AlSi<sub>3</sub>O<sub>10</sub>)(OH)<sub>2</sub> (the coarseness of 0.2...-1.6 mm), potassium KAlSi<sub>3</sub>O<sub>8</sub> and sodium-calcium (80 %  $NaAlSi_3O_8 + 20$  % CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) feldspars, as well as rock-forming minerals, specifically, aegirine NaFeSi<sub>2</sub>O<sub>6</sub> (the coarseness of -0.15 mm) and clay of Quaternary (the Uraguba deposit, the Kola PEN) were used in this work. In addition, three samples were investigated that contained soil humus and that were taken out from forest litter (the accumulative horizon with the greatest content of humus), from podsolic eluvial (the washout soil) and illuvial (the wash-in soil) horizons, the respective samples 1, 2, and 3.

TABLE 2						
Variation of the concentration	of cesium a	and strontium	in the solution	without a	background	over time

Number Cation of the soil sample			entra			nol/l) ne, days	SEC, mg-eq/g	$K_{\rm d}$ , ml/g
		0.5	1	2	4	6		
1	Cs	2.9	1.6	1.0	0.9	0.9	0.0244	271
	Sr	2.8	1.6	1.1	1.1	1.1	0.0472	214.5
2	Cs	4.8	4.4	1.8	1.4	1.4	0.0224	160
	Sr	6.3	4.9	2.8	2.2	2.2	0.0384	87.3
3	Cs	5.8	4.6	3.0	2.4	2.5	0.0180	72
	Sr	5.2	4.2	3.1	2.9	2.9	0.0328	56.6

Sorption was conducted from water solutions containing <sup>134</sup>Cs or <sup>90</sup>Sr radionuclides, or from solutions containing additionally 0.5 M NaCl. Water solutions or solutions with 0.5 M NaCl were used for desorption. Hydrogen ion concentration was adjusted by adding HCl.

## **RESULTS AND DISCUSSION**

# Investigation by chemical method

Sorption and desorption of cesium and strontium by humus-containing samples of prosaic soils have been studied by a chemical method. Table 2 lists data into kinetics of sorption, on sorption exchange capacity (SEC) and on the distribution constant  $K_d$ .

The  $K_{\rm d}$  magnitude was determined from the ratio  $K_{\rm d} = (A_{\rm S}/A_{\rm L})\alpha$ , where  $A_{\rm S}$  and  $A_{\rm L}$  are the fractions of radionuclides in solid and liquid phases respectively from those initial, %;  $\alpha$  is the ratio of the volume of the solution to the mass of the solid phase, cm<sup>3</sup>/g.

It is evident from the data of Table 2 that saturation by cesium or strontium is achieved after approximately 2 days, and the SEC of strontium is approximately 2 times higher as compared to cesium. This bears indirect witness to the fact that either cesium appears capable to occupy only about a half of cation-exchange

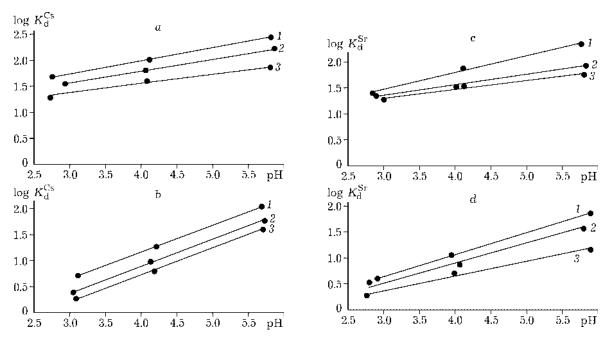


Fig. 1. Dependence of cesium (a, b) and strontium (c, d) sorption degree by samples from water solution (a, c) and from water solution containing 0.5 M NaCl (b, d) on the pH: 1-3 – the samples 1-3, respectively.

TABLE 3 Desorption of cesium and strontium cations by water solutions of two different compositions (pH 1, L:S=40, desorption time is 1 h)

Sample	Cation	$A_{ m L},~\%$	$A_{ m S},~\%$	$K_{\rm d}$ , ml/g	$\logK_{ m d}$
number					
		The	e Solution of	0.1 M HCl	
1	Cs	78.1	21.9	11.2	1.05
	Sr	82.8	17.2	8.3	0.92
2	Cs	77.4	22.6	11.7	1.07
	Sr	79.2	20.8	10.5	1.02
3	Cs	68.7	31.3	18.2	1.26
	Sr	83.4	16.6	8.0	0.90
		The Solu	tion of 0.1 M	M HCl + 0.5 M N	aCl
1	Cs	99.4	0.6	0.24	-0.62
	Sr	98.2	1.8	0.73	-0.14
2	Cs	99.2	0.8	0.32	-0.49
	Sr	98.4	1.6	0.65	-0.19
3	Cs	98.7	1.3	0.53	-0.28
	Sr	98.7	1.3	0.53	-0.28

vacancies, or strontium is sorbed as a single-charged cation.

Figure 1 displays the calculated values of the dependence of  $K_{\rm d}$  for cesium and strontium on the pH in the course of sorption from water solutions and from solutions that contain additionally 0.5 M NaCl. It is evident that 0.5 M NaCl that is available in the solutions substantially hinders sorption of cesium and strontium. In addition, sorption considerably worsens upon an increase in the acidity of the solutions, which is related to an increased competition of sodium and hydrogen ions with respect to cesium and strontium cations during the course of sorption.

Upon extrapolation of the obtained results to cover the pH values that correspond to acid solutions, an assumption can be made that podsolic soils that are saturated by cesium or strontium will "be washed out" of cations of the mentioned elements by acid solutions that contain sodium. From Fig. 1 it is evident that, when the solution contains 0.5 M NaCl,  $\log K_{\rm d}^{\rm Cs} = \log K_{\rm d}^{\rm Sr} = 0$  at pH  $\geq$  1, *i.e.* the concentration of monoprotic acid in the solution that is equal to 0.1 mol/l is sufficient for effective desorption.

Based on the data acquired, desorption processes by solutions of two compositions have been studied. In the first case, the solution contained 0.1 M HCl; in the second, it contained 0.1 M HCl and 0.5 M NaCl.

The results of the experiments are presented in Table 3. It is evident that desorption of cesium and strontium cations proceeds rather completely and quickly, especially when used a solution that contained 0.1 M HCl and 0.5 M NaCl.

## Investigation by radiometric method

Table 4 lists the data of radiometric investigations. It has been found that phlogopite sorbs main part of cesium for the first 3 h, whereas cesium sorption by muscovite has a more complex nature. During the course of further standing, desorption occurs in the solution that is possibly related to hydrolytic passing of potassium cations into solution, these cations promoting temporary desorption of cesium. When hydrolytic destruction of the surface layers of muscovite is completed, cesium cations fill the formed sorptionally active positions. An assumption can be made that a decrease in the sorption activity of Na-Ca spar in the course of time is also related to a complicated influence of sodium cations that are incorporated in the spar on the process of cesium sorption.

Cesium sorption by K-Mg spar reaches the maximum approximately after 6 days, sorption

TABLE 4 Kinetics of sorption of  $^{134}\mathrm{Cs}$  and  $^{90}\mathrm{Sr}$  radionuclides by samples of minerals and soil

Mineral, soil	eral, Cation	Amount of radionuclides that is absorbed from the solution (%) after the contact time, $h$											
		3	24	48	66	72	98	136	146	170	192	240	288
Phlogopite	<sup>134</sup> Cs	35.5	30.1	29.9	-	30.7	-	-	34.4	39.1	-	40.2	_
	$^{90}\mathrm{Sr}$	-	48.5	-	-	-	58.0	-	-	-	64.7	-	68.1
Muscovite	$^{134}\mathrm{Cs}$	17.4	13.1	5.8	_	9.2	-	-	8.0	6.8	-	14.7	_
	$^{90}\mathrm{Sr}$	-	61.5	-	_	_	71.3	_	_	-	72.8	-	72.2
K-Mg spar	$^{134}\mathrm{Cs}$	15.8	18.1	23.0	_	27.5	_	_	32.6	29.0	_	30.2	-
	$^{90}\mathrm{Sr}$	-	67.8	-	_	_	81.8	_	_	-	79.0	-	77.5
Na-Ca spar	$^{134}\mathrm{Cs}$	22.4	25.0	22.4	_	22.9	-	_	21.8	17.7	_	17.3	-
	$^{90}\mathrm{Sr}$	-	56.7	-	_	-	62.6	-	-	-	65.1	-	65.8
Aegirine	$^{134}\mathrm{Cs}$	38.0	65.4	73.8	_	76.4	-	-	80.2	78.4	-	78.5	-
	$^{90}\mathrm{Sr}$	-	69.3	-	_	_	82.5	_	_	-	83.6	-	84.6
Clay	$^{134}\mathrm{Cs}$	66.9	90.5	96.0	_	94.4	-	_	98.6	96.4	_	97.8	-
	$^{90}\mathrm{Sr}$	-	89.3	-	_	_	90.4	_	_	-	92.3	-	90.7
Sample 1	$^{134}\mathrm{Cs}$	-	_	-	85.3	_	_	90.7	_	-	_	-	-
	$^{90}\mathrm{Sr}$	-	_	-	89.8	_	_	_	_	-	96.0	-	-
Sample 2	$^{134}\mathrm{Cs}$	-	-	-	83.2	_	_	83.2	_	-	-	-	-
	$^{90}\mathrm{Sr}$	-	-	-	77.6	_	_	_	_	-	93.8	-	-
Sample 3	$^{134}\mathrm{Cs}$	-	-	-	63.4	_	_	66.1	_	-	-	-	-
	$^{90}\mathrm{Sr}$	_	_	_	87.6	_	_	_	_	_	90.5	_	_

Note. The dash implies that the measurements not available.

by aegirine and podsolic soil samples, after 3 days, and sorption by clay, after 1 day.

It has been found that aegirine sorbs cesium in a greater quantity in comparison with micas and feldspars. The greatest sorption activity is evidenced for clay, which agrees with numerous literary data. Strontium is sorbed by micas,

TABLE 5 Distribution constant  $K_{\rm d}$  for sorption of cesium and strontium radionuclides by samples of minerals and soils, ml/g

Mineral,	Sorption	<sup>134</sup> Cs	<sup>90</sup> Sr	
soil	time, h			
Phlogopite	240	48.2	11.6	
Muscovite	240	14.6	39.1	
K-Mg spar	240	18.4	12.1	
Na-Ca spar	240	6.6	3.6	
Aegirine	240	120	83	
Clay	240	1034	466	
Sample 1	66	391	150	
Sample 2	66	198	136	
Sample 3	66	77	80	

feldspars, aegirine, and by samples that contain humus more effectively as compared to cesium. Clay sorbs strontium rather effectively, but somewhat weaker than does cesium.

Table 5 gives the calculated values  $K_{\rm d}$  of cesium and strontium radionuclides for the studied minerals and soils.

For humus-containing podsolic soils, the values  $K_{\rm d}$  for cesium and strontium that have been received by chemical and radiometric methods (see Tables 2 and 5) are comparable, although the concentration values of  $^{134}{\rm Cs}$  and  $^{90}{\rm Sr}$  in solutions, when the measurements were made by the radiometric method, were some orders less relative to the measurements in the solutions that were used with chemical method. This suggests that, first, the employed research methods have made it possible to obtain reliable results, and second, the sorption regularities were valid over a wide change in the concentration of sorbed cations in the solutions.

The analysis of experimental data on the kinetics of desorption of <sup>134</sup>Cs radionuclide by

TABLE 6 Kinetics of desorption of  $^{134}\text{Cs}$  cations by water solution that contains 0.1 M HCl + 0.5 M NaCl ( L : S = 40)

Mineral,	Amount	of radionuc	lide that has passed					
soil	into solut	into solution (%) upon the contact time, h						
	1	3	22					
Phlogopite	63.6	80.2	94.1					
Muscovite	100	100	100					
K-Mg spar	81.6	100	100					
Na-Ca spar	89.9	91.2	98.1					
Aegirine	84.3	96.8	100					
Clay	32.8	42.8	53.6					
Sample 1	78	90	96.1					
Sample 2	65.1	79.4	81.2					
Sample 3	40.3	46.3	80.0					

water solution containing 0.1 M HCl + 0.5 M NaCl (Table 6) implies that the easier passes the process of sorption of radionuclides, the more difficult their desorption can be realized. However, when the solution of the suggested composition is used for desorption, 53.6 % of the sorbed  $^{134}\mathrm{Cs}$  radionuclide has passed from clay into the solution even from the strongest associates with clay. Analogous results have been also received for desorption of  $^{90}\mathrm{Sr}$  radionuclide from the studied samples of minerals and soils.

Table 7 presents the values  $K_{\rm d}$  that have been calculated from experimental data for cesium and strontium radionuclides. When analyzing these data, allowance should be made that no equilibrium was attained sometimes

during the desorption and the  $K_d$  values may increase for some samples in the course of time.

Desorption of <sup>134</sup>Cs from quarternary clay proceeds most difficultly; it is easier from humus-containing samples of podsolic soils. Desorption of <sup>134</sup>Cs radionuclides from the majority of the studied minerals passes rather completely and quickly, being somewhat slower for phlogopite.

Desorption of  $^{90}$ Sr radionuclide passes for more than 90 % even during the first 24 h, this process being realized in a more complicated manner in the case of quarternary clay and the sample 1 (with the greatest content of humus).

# Flow diagram for deactivation of soils

Desorption of cesium radionuclides from the majority of minerals (except for clay of Quaternary) and from the studied samples of humus-containing soils by a solution that contains 0.1 M HCl  $\pm$  0.5 M NaCl passes just for 3 h. The degree of strontium desorption from all the studied samples with the contact time of 24–26 h exceeded 90 %. It is likely that it is possible to reach a preset completeness of cesium desorption from clay with the countercurrent process.

The data acquired and the experiments that have been performed previously [9–11] make it possible to suggest a process flow diagram for deactivation of soils (Fig. 2).

TABLE 7 Distribution constants  $K_{\rm d}$  during desorption of cesium and strontium radionuclides

Mineral,	$^{134}\mathrm{Cs}$			$^{90}\mathrm{Sr}$		
soil	Time, h	Desorption	$K_{\rm d}$ , ml/g	Time, h	Desorption	$K_{\rm d}$ , ml/g
		degree, %			degree, %	
Phlogopite	22	94.1	2.5	26	93.4	2.8
Muscovite	22	100	0	26	93.5	2.8
K-Mg spar	22	100	0	26	93	3.0
Na-Ca spar	22	98.1	0.8	26	92.8	3.1
Aegirine	22	100	0	26	96.2	1.6
Clay	22	53.6	34.6	24	90.2	4.4
Sample 1	22	96.1	1.6	24	90.7	4.1
Sample 2	22	81.2	9.3	24	94.6	2.3
Sample 3	22	80.0	10.0	24	95.5	1.9

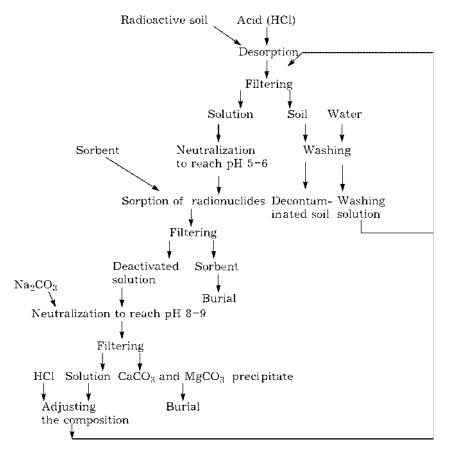


Fig. 2. Process flow diagram for soil deactivation.

The suggested method is based on the ability of  $TiOHPO_4 \cdot nH_2O$  sorbent for a selective absorption of cations of heavy radionuclides from solutions that contain a large excess of lighter cations of alkaline and alkali-earth elements that are competitive and similar in their chemical properties. The specific radioactivity of the sorbent that is saturated by radionuclides comprises as much as  $10^4$  Bk/g [9, 10]. Upon the calcination at a temperature of 600-650 °C, the sorbent mass decreases almost 2 times. The formed binary phosphates of radionuclides and titanyl are almost insoluble in slightly acidic or alkalescent water solutions [11].

To realize the suggested method, it is necessary to perform the following operations: desorption of radionuclides from soil by an acidified NaCl solution; neutralization of the solution containing radionuclides by soda to reach an optimum pH value (4–5); selective sorption of radionuclides from the leaching solution by  $\text{TiOHPO}_4 \cdot n\text{H}_2\text{O}$  sorbent; transformation of calcium and magnesium into carbonates and their excretion from the deactivated solution (in the

case that soil contains carbonatites); adjusting the composition of the deactivated solution with the aim of re-using to desorb radionuclides.

Upon neutralization of muriatic acid by soda to reach pH 7, chloride solutions contain 19.2 g/l NaCl. Low (11.65 g/l) content of chlorine anion in the solutions that are used for desorbtion makes it possible to wash easily the deactivated soil by water, if necessary, to attain the level that does not lead to the pollution of subsoil waters higher than the admissible norms.

The number of cycles to perform the desorption depends on the initial level of radioactive pollution of soil and on the mineral composition of the soil.  $TiOHPO_4 \cdot nH_2O$  sorbent can be made in the form of powder or granules [12] and thus be used both under static, and dynamic regimes.

# CONCLUSION

Hence, the suggested technology can be realized with the use of standard chemical

processing equipment, with no formation of harmful wastes and exhausts. With its use, radionuclides are concentrated in a product with high activity that is stable in a long-term storage, which makes it possible to reduce the expenses for their storage to the maximum extent.

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