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Speciation of U, Pu, and fission products in soils of radioactive waste disposal

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About 500,000 cubic meters of radioactive waste with the total activity of $4.8 \cdot 10^{14}$ Bq are concentrated in the "Ryzhyi Les" disposal of the Chornobyl Exclusion Zone. This disposal represents a high environmental risk in case the radioactive waste is flooded with ground water.

More than 99% of U and Pu of fuel origin are concentrated in a 0-2 cm upper soil within the Exclusion Zone. An atomic ratio for $^{236}U/^{235}U$ ranges from 77.7 to 124.3, which is essentially different from the natural ratio (137.8). The activity ratio of even isotopes $^{234}U/^{238}U$ in the investigated soils is increased as compared to the natural one and reaches up to 1.5-3.7. The Pu content in soils and its isotopic composition ($^{239}Pu/^{240}Pu$, $^{240}Pu/^{241}Pu$) is at the similar level as the data calculated for nuclear fuel that was irradiated in the reactor between 0.7 and 1.7 year.

The speciation of $^{239+240}Pu$, ^{90}Sr, and ^{137}Cs has been studied using the sequential leaching, dialysis and electrodialysis methods. Migration of $^{239+240}Pu$ is dominated by pseudo-colloid forms, of ^{90}Sr – by the ionic ones, and of ^{137}Cs – both by the ionic and pseudo-colloid species. The $^{239+240}Pu$ anionic species, the ^{137}Cs cationic forms are dominated in ionic species. The 90Sr anionic and cationic species are equally distributed in the ionic fraction.

The obtained data show that phase transformation $UO_2 \rightarrow U_3O_8$ took place during the emergency release of uranium fuel from the reactor.

Introduction

Two main groups of artificial radionuclides can be distinguished in the spectrum of the Chornobyl release. Fission products and ^{236}U form the first group. All elements of this group are presented in the earth's crust by appropriate natural stable or radioactive analogues, which geochemistry is mainly studied. This fact has been facilitated forecasting of their migration in the hyper-genesis zone. The second group comprises transuranium elements that haven't natural bearers and are practically unstudied from the geochemical point of view.

Sources of radioactive waste within the Chornobyl Exclusion Zone are presented by radioactive contaminated soils, wood (biomass), constructions, mechanisms, etc. Most of these materials are stored in more than 800 temporary radioactive waste localization sites, which were created in force-majeure (1986-1987) out of line with normative-technical requirements [1].

Total volume of temporary radioactive waste disposal facilities within Chornobyl Exclusion Zone, reaches 2,040,000 cubic meters (2,310,000 tons) containing $7{,}3 \cdot 10^{15}$ Bq of radioactive waste. Insufficient isolation, and possibility underflooding of these sites may cause radionuclide migration into the subterranean waters and the Dnieper basin that threaten with environment radioactive contamination [3].

250,000 tons (500,000 cubic meters) of radioactive waste with total activity of $4.8 \cdot 10^{14}$ Bq is concentrated in the "Ryzhyi Les" disposal site covering the area over 2 sq.km. The disposal site is stored to the south of the Pryp'yat town in 3 km to the west of Chornobyl NPP. 49 depots of trench type and 8 of "clamp" type were created at the first section of the disposal. The disposal site comprises radioactive contaminated soils, dead wood, cottage constructions. 32 trenches are underflooded during floods. This disposal site is the most dangerous one taking into account underflooding of radioactive waste with underground water.

Study of the Pu migration ability in the zone of Chernobyl accident influence have been limited with the data of its quantitative content in various environmental objects [2, 5], but it is not related to the radionuclides chemical condition in the water soluble form. Such geochemical information is necessary for long-term forecasting of Pu isotopes behavior in hyper-genesis zone, increasing of radioactive waste localization reliability in the nuclear-waste disposal sites, working out of water purification technologies, etc.

Methods

The $^{239,240}Pu$ and ^{236}U leaching from natural specimens have been studied using the isotope-indicated method.

The conjugated study of U and Pu has been carried out on the basis of the next prerequisites:

1. Among the elements contained in the earth crust, U is the most similar analogue of Pu. This

way seems to be very promising inasmuch as chemistry of U has been closely studied.

2. Inasmuch as ^{236}U like Pu isotopes is formed in a reactor by the reaction of neutron capture, one can expect that speciation of these elements in the nuclear fuel is to be similarly.

Quantitative determination of U and Pu is made by the isotopic dilution method at the mass spectrometer and -spectrometer consequently. Standard solutions of ^{236}Pu, ^{242}Pu and ^{232}U have been used as isotopic markers.

Isotopic markers ^{232}U and ^{236}Pu have been carried in the solution at the beginning of soils leaching. After leaching two aliquots have been bleeded from the solution and purified by ultra filtration. U have been precipitated by the radiochemical and electrolytical methods and analyzed at the α-spectrometer for $^{238}U/^{232}U$ and $^{234}U/^{238}U$ ratios determination. Than U was washed off the target for the $^{238}U/^{235}U$ and $^{235}U/^{236}U$ ratios mass spectrometric measuring.

For the quantitatively determination of ^{232}U, ^{235}U, ^{236}U, ^{238}U, ^{236}Pu, ^{238}Pu, and $^{239+240}Pu$, the marker of ^{242}Pu and tracer $^{238}U/^{235}U=0.1022$ have been brought in the second aliquot. After radiochemical separation and purification, U was analyzed by mass spectrometric, and Pu was analyzed by α-spectrometric methods for $^{236}Pu/^{242}Pu$, $^{239+240}Pu/^{242}Pu$, and $^{238}Pu/^{239+240}Pu$ ratios determination.

Water-soluble and exchangeable species of $^{239,240}Pu$ have been determined using the method of soils consecutive leaching with distilled water and 1 M solution of ammonium acetate. The ratio between solid and liquid phases is made up as 1 to 5. Separation of ionic and pseudo-colloid forms, anionic and cationic ones have been investigated using the dialysis and electrodialysis methods.

Results and Discussion

More than 99% of U and Pu within the Chernobyl Exclusion Zone have been accumulated in the higher stratum of soils with the thickness of 2 cm (Table 1). Hand-to-mouth migration ability of these elements is conditioned with insoluble form of radioactive fallouts presented by the hot particles of fuel origin that allows us to use only the upper soils and bottom sediments in the further investigations. Nuclear fuel ejection in the environment is proved by the data of uranium isotopic composition in the soils. $^{238}U/^{235}U$ ratio in the upper soils within the Chornobyl Exclusion Zone considerably differs from the natural value (137.8) [6].

$^{238}U/^{235}U$ ratio in soils and bottom sediments varies between 77.7 and 124.3 (Table 2) that is conditioned on the ratio of released uranium isotopes of nuclear fuel origin, natural U content in soils, and degree of ^{235}U burning-out in the emergency reactor.

Ratio of even uranium isotopes ($^{234}U/^{238}U$) is increased to 1.5-3.7 that is also higher than natural values. At the same time the total content of U in soils does not exceed the normal Clarke values testifying to insignificant desaturation of natural U by the U of fuel origin.

Table 1

Vertical distribution of U and Pu isotopes of technogeneous origin in the soils (6 samples) within the Chernobyl Exclusion Zone.

Soil stratum, cm	$^{239}Pu + ^{240}Pu$, %	$^{238}U/^{235}U$, atomic units
0-1	92.0-96.7	79.9-103.5
	93.9	91.3
1-2	2.9-7.9	126.7-135.8
	5.5	112.5
2-3	0.3-0.6	134.7-137.3
	0.45	136.1
3-4	0.0-0.2	137.1-137.8
	0.12	137.5
4-5	0.0-0.1	137.6-137.8
	0.03	137.7

Note: in this table and those below: in numerator – limiting value, in denominator – simple mean.

Data of Pu content and its isotopic composition ($^{239}Pu/^{240}Pu$; $^{240}Pu/^{241}Pu$) are in good accordance with the data calculated for 2% concentrated nuclear fuel, which lying in the reactor is limited with the time slice in 0.7-1.7 year. This fact testifies to reception of the nuclear fuel with the average depth of burnout into environment. At the same time $^{239}Pu/^{236}U$ ratio is between 1.23 and 0.53. These data are typical not only for the average depth of burnout but also are higher than those for spent fuel. The latter fact is in conflict with the data of U isotopic composition for the number of analyzed natural samples. We haven't obtained values of $^{238}U/^{235}U$ ratio exceeding 137.8. But this ratio for spent fuel is made up to 214.9. Thus the only one explanation of the ^{239}Pu deficiency in comparison with ^{236}U is existence of emergency nuclear process, which is cardinally distinguished from the theoretically calculated one for the reactor working in the normal mode.

Table 2

Isotopic composition ant content of U and Pu in soils and bottom sediments within the Chernobyl Exclusion Zone

	Soils (11 samples)	Bottom sediments (4 samples)
$^{238}U/^{235}U$ (in atomic units)	77,7-124,3 94,1	86,6-121,9 99,1
$^{235}U/^{236}U$ (in atomic units)	8,9-76,7 22,6	27,9-122,0 55,1
$^{234}U/^{238}U$ (in units of activity)	1,5-3,7 2,6	1,5-2,3 2,0
U total content, 10^{-6} g per g	0,76-3,06 1,78	0,83-1,60 1,16
$^{239}Pu/^{240}Pu$ (in atomic units)	2,3-5,3 4,2	4,5-4,9 4,7
$^{240}Pu/^{241}Pu$ (in atomic units)	2,3-5,4 4,2	4,3-4,6 4,5
$^{238}Pu/^{239+240}Pu$ (in units of activity)	0,43-0,51 0.47	0,47-0,50 0,49
$^{239+240}Pu$, Bq per kg	500-12,500 4,400	460-1,100 840

Taking into account importance of forecasting of ^{239}Pu and ^{240}Pu migration ability and possibility of groundwater contamination, we have studied the component composition of Pu water-soluble forms in the soils of "Ryzhyi Les" radioactive waste disposal site (Table 3).

The portion of water-soluble species increases with the depth of a disposal. This portion increases due to the $^{239+240}Pu$ specific activity value rising. The correlation coefficient (R) between these values is about 0.75.

Table 3

Contents and componential composition of water-soluble $^{239+240}Pu$ in the soils of the "Ryzhyi Les" radioactive waste disposal site

Number of disposal trench	Sampling depth, m	$^{239+240}Pu$ content in soil, Bq per kg	Water-soluble $^{239+240}Pu$, %	Componential composition of water-soluble $^{239+240}Pu$, %			
				Ionic			Pseudo-colloid
				Total	Cationic	Anionic	
202	0,6-0,9	1500	0,4	33	5,9	27,1	67
203	1,5-1,8	1100	2,2	10	0,2	9,8	90
203	2,4-2,7	30 000	3,2	28	4,2	23,8	72
204	2,1-2,4	13 000	1,4	17	1,2	15,8	83
205	1,5-1,8	2300	0,7	44	10,6	33,4	56
206	0,9-1,2	10 000	1,2	41	8,2	32,8	59
208	1,2-1,5	2700	0,7	16	1,3	14,7	84

Chemical migration of $^{239+240}Pu$ is realized at the expense of pseudo-colloid forms (56-96 %). At the same time 76-98 % of ionic forms are presented by anions (Table 6). When the total content of ionic forms is increased, the role of cationic ones is raised. So, only 10% of water-soluble $^{239,240}Pu$ in the trench Nr 203 at the depth 1.5-1.8 m corresponded to ionic species, and only 0.2 % to cations. In the trench Nr 205, the part of ionic species increased to 44 %, accordingly, percentage of cationic ones raised to 33 %. The $^{239+240}Pu$ speciation is characterized with the high correlation between values of total ionic, cationic, anionic and pseudo-colloid species contents. The module of R between these values is 0.99.

The ^{90}Sr portion in the water-soluble fraction depended on the radionuclide specific activity (R=0.79). The ^{90}Sr occurrence in this fraction was generally related to ionic species (Table 4). Between 20 and 70 % of ionic species corresponded to cationic forms, the rest is related to anionic species (Table 6). On the average the ionic species are equally distributed between cationic and anionic ones. The portion of cationic species is raised due to the depth of sampling (R=0.75).

The water-soluble ^{137}Cs contents corresponded to ionic species were between 11 and 67 % (Table 5). The part of pseudo-colloid species reached 90 %. Up to 99 % of ionic species corresponded to cationic forms (Table 6).

The high correlation (R between 0.84 and 0.88) is observed between values of $^{239+240}Pu$, ^{90}Sr, and ^{137}Cs specific activity in the corresponding samples that testify to the fuel origin of disposal body contamination. Due to high correlation (R=0.82) between the Nr of trench and ^{137}Cs, and ^{90}Sr ionic and pseudo-colloid species contents, one can concluded that the speciation of these radionuclides is dependent on the type and properties of the disposal body.

The significant correlation is observed between speciation of all studied radionuclides. Module of R between values of total ionic, cationic, anionic, and pseudo-colloid radionuclides species content is between 0.65 and 0.8. This fact testifies to common mechanism of different radionuclides speciation in the disposal body determined by the physical-chemical properties of fuel particles. This mechanism is corresponded to the solid-phase diffusion in the fuel particles that is the limitative stage of the radionuclides water migration [4].

Table 4

Content and componential composition of water-soluble ^{90}Sr in the soils of "Ryzhyi Les" radioactive waste disposal site

Number of disposal trench	Sampling depth, m	^{90}Sr content in soil, Bq per kg	Water-soluble ^{90}Sr, %	Componential composition of water-soluble ^{90}Sr, %			
				Ionic			Pseudo-colloid
				Total	Cationic	Anionic	
202	0.6-0.9	$1.1 \cdot 10^5$	0.63	98.0	19.6	78.4	2.0
203	1.5-1.8	$4.1 \cdot 10^5$	2.6	98.4	68.9	29.5	1.6
203	2.4-2.7	$1.1 \cdot 10^6$	16	97.6	54.7	42.9	2.4
204	2.1-2.4	$4.9 \cdot 10^5$	2.25	98.3	70.8	27.5	1.7
205	1.5-1.8	$4.2 \cdot 10^4$	7.85	95.2	31.4	63.8	4.8
206	0.9-1.2	$9.3 \cdot 10^5$	13	96.2	35.6	60.6	3.8
208	1.2-1.5	$1.5 \cdot 10^5$	3.9	95.3	30.5	64.8	4.7

Table 5

Content and componential composition of water-soluble ^{137}Cs in the soils of "Ryzhyi Les" radioactive waste disposal site

Number of disposal trench	Sampling depth, m	^{137}Cs content in soil, Bq per kg	Water-soluble ^{137}Cs, %	Componential composition of water-soluble ^{137}Cs, %			
				Ionic			Pseudo-colloid
				Total	Cationic	Anionic	
202	0.6-0.9	$1.5 \cdot 10^5$	0.65	66.7	66.4	0.3	33.3
203	1.5-1.8	$8.9 \cdot 10^5$	0.21	64.3	62.6	1.7	35.7
203	2.4-2.7	$2.3 \cdot 10^6$	0.29	52.4	51.7	0.7	47.6
204	2.1-2.4	$7.0 \cdot 10^5$	0.08	47.4	46.5	0.9	52.6
205	1.5-1.8	$4.2 \cdot 10^4$	0.25	23.1	22.8	0.3	76.9
206	0.9-1.2	$1.3 \cdot 10^6$	0.05	11.4	10.6	0.8	88.6
208	1.2-1.5	$1.9 \cdot 10^5$	0.23	28.6	27.7	0.9	71.4

Table 6

The composition of radionuclides ionic species from water soluble fraction, %

Radio-nuclide	Cationic species	Anionic species
$^{239+240}Pu$	7—24/13.4	76—98/86.6
^{90}Sr	20—72/45.7	30—80/54.3
^{137}Cs	93—99/97.5	0.4—7.0/2.5

Conclusions

The $^{238}U/^{235}U$ isotopic ratio is considered to be a sensitive indicator of U of nuclear fuel origin reception into the environmental objects (soils, bottom sediments).

Insignificant quantity of uranium fuel with the average depth of burnout is receipted into environment from the emergency unit of Chernobyl Nuclear Power Plant. This fuel has been accumulated at the soil and bottom sediments surface. After decontamination actions it was transferred to the radioactive waste disposals.

During the emergency release, probably under the influence of high temperature and oxidation-reduction conditions inside the emergency reactor, phase transformation of uranium fuel has taken place being accompanied by the reaction $UO_2 \rightarrow U_3O_8$.

Chemical migration of $^{239+240}Pu$ is realized at the expense of pseudo-colloid forms. Overwhelming quantity of ionic species is presented by anions. When total content of ionic species is increased the role of cationic ones is raised.

Chemical migration of ^{90}Sr is realized at the expense of ionic species. Anionic and cationic species are equally distributed in this fraction. The portion of cationic species is raised due to the depth of sampling.

Chemical migration of ^{137}Cs is realized both by the ionic and pseudo-colloid species. The main part of ionic species is corresponded to cations.

The speciation of $^{239+240}Pu$, ^{90}Sr, and ^{137}Cs is going to the common mechanism determined by the physical-chemical properties of fuel particles contaminating the disposal body.

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Около 500 000 м³ в радиоактивных отходов общей активностью $4.8 \cdot 10^{14}$ Бк сосредоточено в хранилище "Рыжий Лес" Чернобыльской зоны отчуждения. Это захоронение представляет значительную опасность для окружающей среды в связи с подтоплением радиоактивных отходов грунтовыми водами.

Более 99 % U и Pu топливного происхождения сосредоточено в верхнем 2-см слое почв Зоны отчуждения. Атомное отношение $^{238}U/^{235}U$ колеблется в пределах 77,7—124,3, что весьма отличается от природного соотношения

(137,8). Отношение активности четных изотопов $^{234}U/^{238}U$ в исследованных почвах выше по сравнению с природным и достигает 1,5—3,7. Содержание Pu в почвах и его изотопный состав ($^{239}Pu/^{240}Pu$, $^{240}Pu/^{241}Pu$) соответствует таковому, рассчитанному для ядерного топлива, время выгорания которого в реакторе 0,7—1,7 г.

С использованием методов последовательного выщелачивания, диализа и электродиализа изучено формообразование $^{239+240}Pu$, ^{90}Sr и ^{137}Cs в образцах захороненных почв. Миграция $^{239+240}Pu$ определяется псевдоколлоидными формами, ^{90}Sr — ионными, ^{137}Cs — поровну ионными и псевдоколлоидными. В составе ионных форм доминируют анионные формы $^{239+240}Pu$ и катионные формы ^{137}Cs. Анионные и катионные формы ^{90}Sr поровну распределены в составе ионных форм.

Полученные данные свидетельствуют, что во время взрыва на IV энергоблоке ЧАЭС происходила фазовая трансформация $UO_2 \rightarrow U_3O_8$.

Близько 500 000 м³ радіоактивних відходів загальною активністю $4.8 \cdot 10^{14}$ Бк зосереджено в сховищі "Рудий Ліс" Чорнобильської зони відчуження. Це захоронення являє значну небезпеку для навколишнього середовища в зв'язку з підтопленням радіоактивних відходів грунтовими водами.

Понад 99 % U та Pu паливного походження зосереджено в поверхневому 2-см шарі ґрунтів Зони відчуження. Атомне співвідношення $^{238}U/^{235}U$ коливається в межах 77,7—124,3, що суттєво відрізняється від природного (137,8). Співвідношення активності парних ізотопів $^{234}U/^{238}U$ вище порівняно з природним та сягає 1,5—3,7. Вміст Pu в грунтах та його ізотопний склад ($^{239}Pu/^{240}Pu$, $^{240}Pu/^{241}Pu$) відповідає такому, розрахованому для ядерного палива, час вигорання котрого в реакторі 0,7—1,7 р.

З використанням методів послідовного вилуговування, діалізу та електродіалізу вивчено формоутворення $^{239+240}Pu$, ^{90}Sr та ^{137}Cs в зразках захоронених ґрунтів. Міграція $^{239+240}Pu$ визначається псевдоколоїдними формами, ^{90}Sr — іонними, ^{137}Cs — порівну іонними та псевдоколоїдними. У складі іонних форм домінують аніонні форми $^{239+240}Pu$ та катіонні форми ^{137}Cs. Аніонні та катіонні форми ^{90}Sr порівну розподілені у складі іонних форм.

Отримані дані свідчать, що під час вибуху на IV енергоблоці ЧАЕС відбувалася фазова трансформація $UO_2 \rightarrow U_3O_8$.