International Journal of Biology and Chemistry 12, № 2, 116 (2019)

IRSTI 87.15.91 https://doi.org/10.26577/ijbch-2019-i2-15

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Species of uranium of the Kamyshanovskoe deposit (Kyrgyzstan)

Abstract: On the territory of Southern Kazakhstan and its adjacent territory of Kyrgyzstan, there is a unique world-wide Betpakdala-Shu-Ili Province, where up to 15% of the world uranium reserves are concentrated. Technological work on the extraction and processing of uranium ores in these deposits began in the middle of the last century, while until the mid-80s mining was carried out by mining in mines and open pits, and from the mid-80s the method of sulfuric acid leaching was used.

Object of this investigation is Kamyshanovskoe uranium deposit, which is located on the territory of Republic of Kyrgyzstan (about 22 km of its capital – Bishkek city). The natural gamma-emitted radionuclides were determined by gamma-spectrometry measurements (“Ortec” HPGe detector) in a core sample collected from the Kamyshanovskoe uranium peat deposit (0-37 cm depth). The results show U isotopes concentration peak at 12 cm, while the concentrations of its progenies are roughly constant down the profile. Thermo-gravimetry analysis (NETZSCH STA 449 F3A–0372–M) showed, the main part of potentially mobile phases (organic matter, clay and carbonates) was located at the surface.

Solid speciation of uranium has been examined in peat samples collected at the Kamyshanovskoe deposit using sequential extraction. Sequential extraction was carried out using the protocol employed by A.Tessier and et al. In all filtrates natural uranium isotopes were measured by a high resolution alpha-spectrometer (“Alpha-analyst”, Canberra) after appropriate radiochemical preparation, consisting of extraction by 30% tributyl phosphate in toluene and electrodeposition on a steel disk with a mixture of 25% solution of ammonium chloride and saturated solution of ammonium acetate as electrolyte solution. Sequential extraction of peat samples clearly showed that most of uranium is in reversibly bound fractions obtained by treatment with ammonium acetate, hydroxylamine with hydrochloric acid and distilled water, indicating high mobilization potential of uranium in this peat.

Key word: uranium isotopes, peat, Kamyshanovskoe deposit, species of uranium isotopes, sequential extraction, thermo-gravimetry analysis

Introduction

The territories of Southern Kazakhstan and adjacent territory of Kyrgyzstan are known as unique uranium provinces. Different sources of uranium are concentrated here. Uranium-238 and it’s decay products, due to potential toxicity, became important theme in environmental investigations [1].

Nowadays the determination of total content of radionuclides became less informative in comparison with data of chemical compounds, which radionuclides are involved in; as hazard of radionuclides depend on their bioavailability and eco-toxicity, which are in strong depend from their chemical forms, or speciation [2]. It is possible to name several interactions, controlling mobilization of uranium in solution. Among them are dissolution, complex formation, and desorption-sorption at the water-rock interface [3-4].

This paper focuses primarily on determination of species of uranium isotopes of the Kamyshanovskoe deposit. In this study, solid speciation of uranium has been examined in peat samples collected at the Kamyshanovskoe deposit using sequential extraction. Sequential extraction was carried out using the protocol employed by A.Tessier and et al. (1979). The obtained data will give basis for prediction of behaviour of uranium isotopes in environment depending on changing conditions.

Materials and methods

2.1 Object description

On the territory of Southern Kazakhstan and its adjacent territory of Kyrgyzstan, there is a unique world-wide Betpakdala-Shu-Ili Province, where up to 15% of the world uranium reserves are concentrated. Technological work on the extraction and processing of uranium ores in these deposits began in the middle of the last century, while until the mid-80s mining was carried out by mining in mines and open pits, and from the mid-80s the method of sulfuric acid leaching was used.

Object of this investigation is Kamyshanovskoe uranium deposit. This uranium peat deposit is located on the territory of Republic of Kyrgyzstan and about 22 km of its capital – Bishkek city. Figure 1 presents the map of the investigated area.

Figure 1 – Location of the Kamyshanovskoe uranium deposit.

The deposit was formed as a result of ground and surface water filtration though peat-bearing materials of Kendyktas mountains following uranium sorption onto organic-rich minerals. The area (1.5 km^2) of Kamyshanovskoe deposit is flat and covered by canes.

The adjacent territory is strong applied by agriculture. Agricultural techniques can be additional reason of uranium release to solution [5]. One of the biggest rivers of the region, Shu river, is located close to deposit. Hence, uranium isotopes and decay products can migrate on long distances.

2.2 Sampling and sample pre-treatment

The core was collected by manually driving polyvinylchloride (PVC) tubes, with diameter of 10 cm, into the peat. The core was promptly transferred to the laboratory. Then, the core was sectioned at 1 cm intervals. The slices were dried at ambient temperature, sieved through 1 mm sieve and homogenized.

2.3 Gamma-ray spectrometry

Gamma-ray spectrometry was done for investigation of uranium-series radionuclides, such as U-238 (measured via ^{234}Th), Ra-226, Pb-210. The slices were sealed to obtain equilibrium of ^{226}Ra with it's progenies to determine their activities by gamma spectrometry. The gamma spectrometric measurements were done by an "Ortec" HPGe detector and the spectra were analysed by "GammaVision-32" programme.

2.4 Thermo-gravimetry analysis

The thermo-gravimetry analysis was done for determination of content of moisture, organic matter, water in clay materials, carbonate dioxide of carbonates. The determination was done by NETZSCH STA 449 F3A–0372–M and analysed by NETZSCH Proteus programm. The determination is based on destruction of main soil components under different temperatures and measuring of mass changing (Table 1) [6].

Table 1 – The temperatures of thermo-gravimetry analysis

Step	Temperature	Component
1	105	moisture
2	350	organic matter
3	600	water of clay materials
4	850	carbon dioxide of carbonates

2.5 Sequential extraction

Uranium speciation in soils was determined by sequential extractions [7]. The analytical procedure is used for the sequential chemical extractions partitioning uranium into seven fractions is presented in Table 2.

Table 2 – The reactants and conditions of sequential extractions

Step	Soil fractions	Corresponding minerals	Used reactant	Procedure
1.	Water soluble	-	MilliQ-water	Shaken for 2 h; centrifuged at 5000 rpm for 30 min
2.	Exchangeable	-	1M NH_4Ac (pH 8.2)	Shaken for 2 h; centrifuged at 5000 rpm for 30 min
3.	Bound to carbonates	Carbonates (calcite, etc.)	1M NH_4Ac (pH 5.0)	Shaken for 2 h; centrifuged at 5000 rpm for 30 min
4.	Bound to Fe-/Mn-oxides	Oxides of iron and manganese (goethite, hematite, perrolusite)	0.04M $NH_2OH{\cdot}HCl$ in 25% (v/v) HOAc	85 ^{0}C; shaken for 5 h; centrifuged at 5000 rpm for 30 min
5.	Bound to organic matter	Organic substances (humus, etc.)	0.02 M HNO_3 and 30% H_2O_2	85 ^{0}C; pH 2 shaken for 5 h; centrifuged at 5000 rpm for 30 min
6.	Strongly bound	Clay minerals (chlorite, kaolinite, etc.)	7 M HNO_3	85 ^{0}C; pH 2 shaken for 6h; centrifuged at 5000 rpm for 30 min
7.	Residual	Terrigenous minerals (quartz, spar, mica)	HF-$HClO_4$	Decompose

The procedure was done with samples of 1.0-1.5 g of initial weight and after each extraction step, samples were centrifuged for 25 minutes at 5000 rpm and supernatants were filtered (0.45 µm). The ratio of solid:liquid was 1:20.

2.6 Alpha-particle spectrometry

In all filtrates natural uranium isotopes were measured by a high resolution alpha-spectrometer ("Alpha-analyst", Canberra) after appropriate radiochemical preparation, consisting of co-precipitation of radionuclides with iron hydroxide, extraction by 30% tributyl phosphate (TBP) in toluene and electrodeposition on a steel disk with a mixture of 25% solution of NH_4Cl and saturated solution of $(NH_4)_2C_2O_4$ as electrolyte solution [8].

Results and discussion

3.1 Concentrations of gamma-emitting radionuclides

The concentration of profiles of ^{238}U, ^{226}Ra, ^{228}Ra, ^{228}Th, ^{210}Pb and ^{40}K are shown in Figure 2.

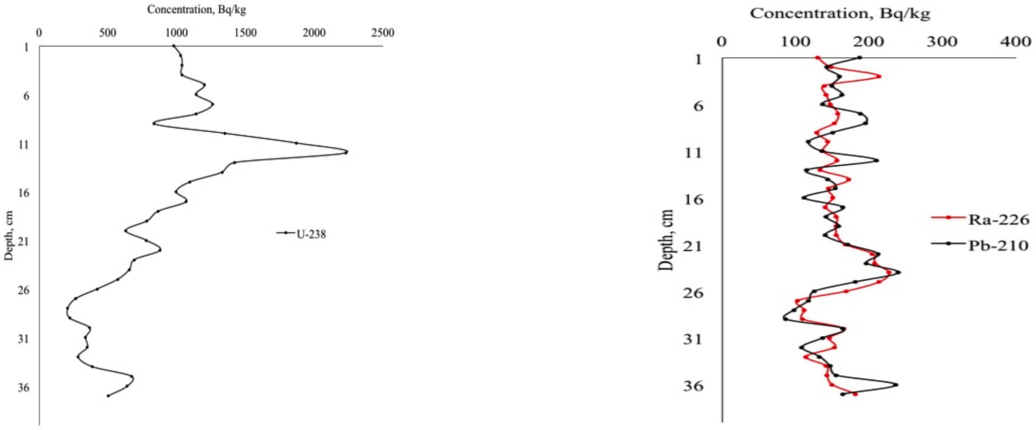
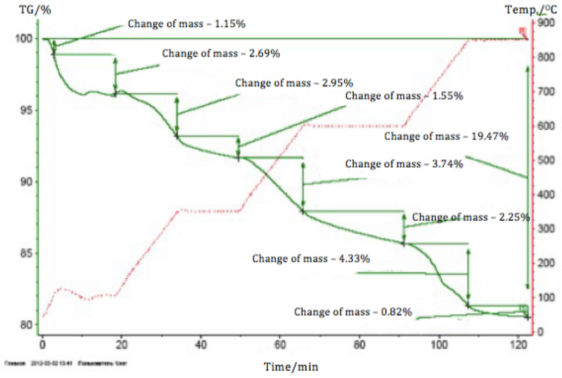


Figure 2 – The uranium series radionuclide`s specific activity profiles (Bq kg^{-1}, dry weight) in peat core.

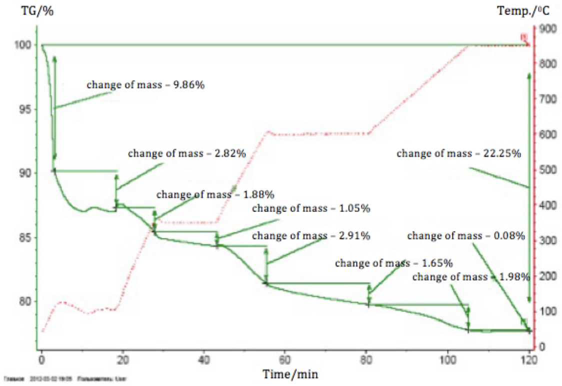
Concentrations of ^{226}Ra and ^{210}Pb are roughly constant with two small peaks found at 3 cm and 27 cm. By contrast, the ^{238}U profile showed a rather constant value down to about 8 cm and then a considerable increase with a maximum at 12 cm. This suggests that uranium migrated down the core with surface waters and accumulated in the depth where the maximum was observed.

3.2 Results of thermo-gravimetry analysis

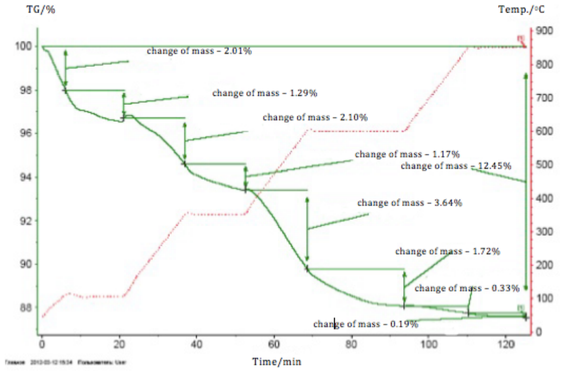
Thermograms of selected core slice samples are presented at the Figure 3.



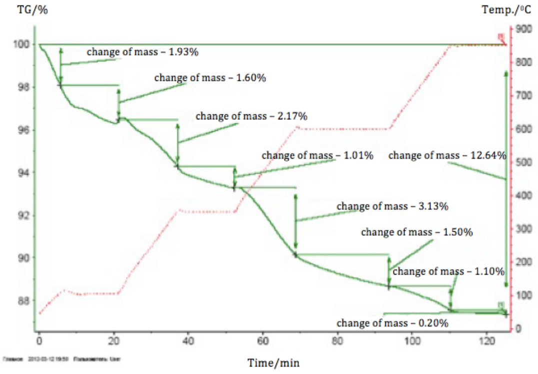
(0-1 cm)



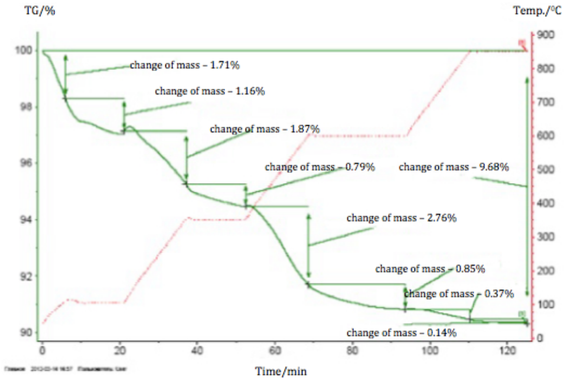
(8-9 cm)



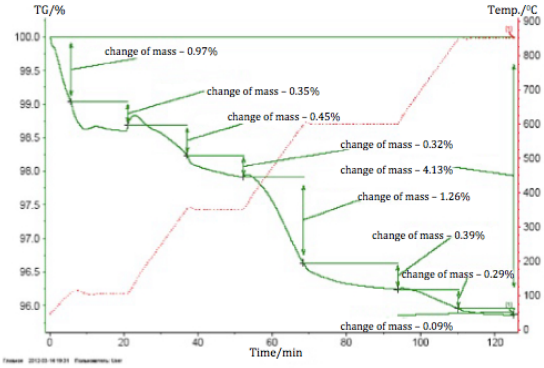
(10-11 cm)



(12-13 cm)



(20-21 cm)



(27-28 cm)

Figure 3 – The thermo-gravimetry analysis of core profiles

The results of thermo-gravimetry analysis showed the decreasing of organic matter down the investigated profiles with maximum amount of organic matter (20.2 mg/g) at the surface (0-1 cm depth). At the depth 8-12 cm, 19-20 and 27-28 cm the concentration of organic matter is 14, 11.8 and 3.1 mg/g, respectively (Table 2).

Table 2 – The results of thermo-gravimetry analysis of the core.

Depth, (cm)	Moisture, (%)	Organic matter,		Clay, (%)	Carbonates, (%)	Total loss of mass, (%)
		(%)	mg/g			
0-1	3.84	4.5	20.21	5.99	5.15	19.47
8-9	12.68	2.94	13.06	4.56	2.06	22.24
10-11	3.3	3.27	14.6	5.36	0.52	12.45
12-13	3.53	3.18	14.16	4.63	1.3	12.64
20-21	2.87	2.66	11.8	3.64	1.23	9.68
27-28	2.09	0.77	3.13	1.67	0.38	4.13

According to results of thermo-gravimetry analysis, the main part of potentially mobile phases (organic matter, clay and carbonates) are located at the surface.

Radionuclides bound to solid samples (soil, peat materials, rock and other) can be desorbed to the liquid phase by changes in soil pH, temperature or oxidation-reduction potential, as well as by the decomposition of soil organic matter, leaching processes, etc. Moreover, the biological availability of metals also depends on the genesis (i.e., source specific characteristics) of the fallout or contamination involved.

3.3 Uranium speciation

The sequential extraction results obtained for the Kamyshanovskoe peat deposit, given in Figure 4, clearly show that most of uranium is in the reversibly bound fractions (in form of carbonates, bound with oxides of iron and manganese and organic fraction), obtained by treatment with NH_4Ac, $NH_2OH{\cdot}HCl$ and H_2O_2, indicating high mobilization potential of uranium in this peat.

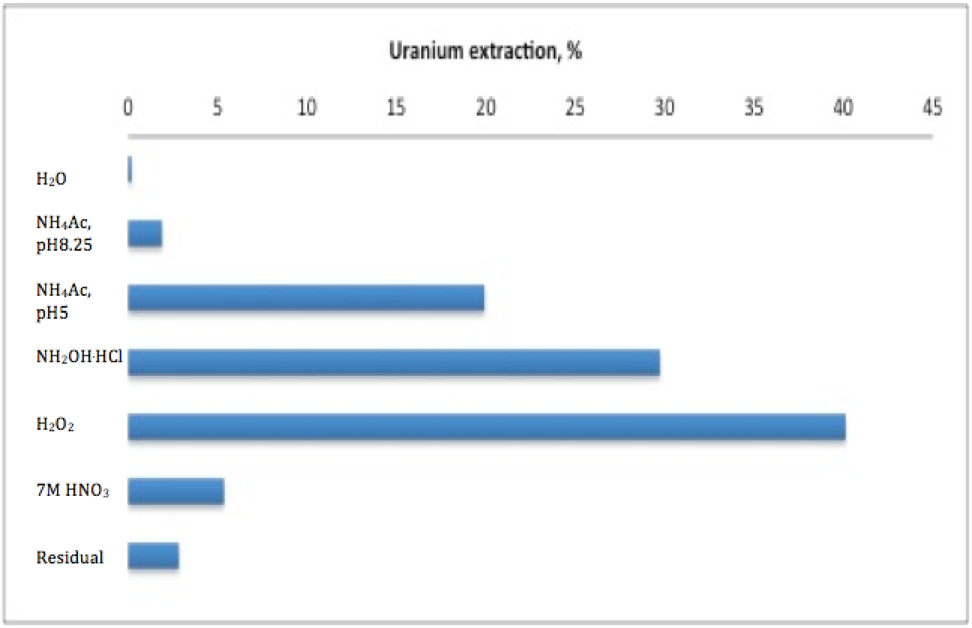


Figure 4 – The partitioning of uranium in soils from Kamyshanovskoe deposit upon sequential extraction analysis

Conclusion

The obtained results of analysing of peat core from the Kamyshanovskoe uranium deposit show a significant variation of uranium series concentrations with depth. The concentrations of main elements are higher than mainly for this region. The uranium concentration in the peat is an order of magnitude higher than the corresponding values of its progenies (^{226}Ra, ^{210}Pb). The highest concentration of ^{238}U was obtained at the at the depth of 12 cm.

Thermo-gravimetry analysis showed, that the main part of potentially mobile phases (organic matter, clay and carbonates) were located at the surface.

Data on the solid partitioning of uranium in peat from the Kamyshanovskoe deposit reveal that about 90 % of uranium was found in potentially mobile forms, indicating potential mobility and availability for plant and other organism uptake.

Acknowledgement

This work was funded under the International Science and Technology Center (ISTC) project (Chu-Rad Project, Contract K-1474).

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