ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

4 (64)

ОКТЯБРЬ – ДЕКАБРЬ 2018 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2018

UDC 504.5

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INVESTIGATION OF SPECIES OF URANIUM ISOTOPES IN AKSHATAU DEPOSIT OF KARAGANDA REGION (KAZAKHSTAN)

Abstract. In this manuscript the species of uranium isotopes in Akshatau deposit of Karaganda region of Kazakhstan are described. Akshatau rare metal deposit is located in the northern part of the Dzungaro-Balkhash geosyncline. By origin, it is Greisenian with molybdenum-tungsten mineralization, genetically associated with an array of leucocratic granites of Permian age.

The species of elements are the most important in studies of investigation of migration ability of contaminants, as well as their bioability and hence bioaccumulation. The knowledge of total content of element is less informative in these questions.

The study of the sequential extraction of uranium isotopes from the waste of the Akshatau deposit, according to A. Tessier protocol, showed that uranium-238 was recorded in the following order: F6 residual > F1 exchangeable > F3 bound to Fe-Mn oxides > F5 acid soluble > F2 bound to carbonates > F0 water-soluble > F4 bound to organic matter; and uranium-234 has the following order: F6 residual > F1 exchangeable > F3 bound to Fe-Mn oxides > F5 acid soluble ≈ F2 bound to carbonates ≈ F0 water-soluble > F4 bound to organic matter.

Keywords: sequential extraction, uranium isotopes, Akshatau, species, migration ability, alpha-spectrometry.

Introduction. Most radioactive isotopes of natural origin include uranium isotopes. Among these are three isotopes of uranium (uranium-238, uranium-235 and uranium-234) and are presented in subsoils in different values of concentration. As a rule, they are located in the deeper layers of the Earth's crust, but as a result of the mining industry, natural radionuclides fall on the Earth’s surface, further spreading over its surface, causing more significant harm to the local population, in the absence of any shielding and radionuclides entering the human body. It is known that minor concentrations of radionuclides, including uranium isotopes, are contained in all minerals, rocks and soils [1]. Soils in the mining industry are usually enriched with radionuclides to levels that are often well above background levels [2].Oxidation of sulphides present in minerals favors leaching of uranium isotopes [3].The migration ability and bioavailability of radionuclides are primarily affected by species of radionuclides. A number of compounds of uranium and its isotopes have increased solubility and, as a consequence, increased migration ability. For Kazakhstan with sufficiently large reserves of natural uranium, today it is extremely important to predict the behavior of uranium isotopes and its accumulation in the human body, especially considering the dense population of the region.

MATERIALS AND METHODS

Object description. Akshatau rare metal deposit is located in the northern part of the Dzungaro-Balkhash geosyncline. By origin, it is Greisenian with molybdenum-tungsten mineralization, genetically associated with an array of leucocratic granites of Permian age. Ore bodies are located in the form of separate sections of their clusters: West, North, North-East, Bulgak, South-West, Central, South-East, Aksai. The main reserves are in the South-Eastern and Central areas, which are mined by the South-Eastern mine, the development of which began in 1941. The main ore minerals are wolframite, scheelite, molybdenite and pyrite.

Sampling. Soil samples for research were sampled at the burial site of the mining and processing complex located near the village of Akshatau of Karaganda region. Soil sampling was carried out based on the results of a preliminary determination of the gamma dose using a portable gamma dosimeter.

Figure 1 – Landfill of tungsten-molybdenum deposit Akshatau

The soil was sampled by a special sampler at a depth of 0–15 cm. The soil was sampled using an envelope method with a side of 10 m. The soil samples obtained from 5 points were combined, fragments of glass, plants, concrete and metals were removed, after which the samples were thoroughly mixed and sealed in plastic bags with preliminary prepared markings [4].

A preliminary assessment of gamma-emitting radionuclides showed the following contents:

^{210}Pb – 4360±260Bq/kg
^{230}Th < 390Bq/kg
^{238}U (via ^{234}Th) – 340±150Bq/kg
^{226}Ra - 5200±160Bq/kg
^{228}Ra < 44 Bq/kg

Sequential extraction. The determination of species of the radionuclides was carried out by the method of sequential selective extraction of minerals from the solid phase of separate groups of compounds soluble in various reagents. To determine the radionuclides in the mineral components of the soil and bottom sediments, a modified sequential extraction method proposed by A. Tessier was used [5]. For carrying out the leaching processes, 1.0 g of a dry sample was investigated, and the ratio of the solid and liquid phases was 1:20. After each extraction, the liquid portion was separated by centrifugation for 25 minutes at 5000 rpm, then the precipitate was washed with 15 ml of distilled water and filtered through membrane filters with a pore diameter of 0.45 μm. The main conditions for performing selective leaching and the necessary reagents are listed in table 1.

Table1–Sequential extraction of radionuclides [5]

Fraction	Reagent	Tempe-rature, ^{0}C	Duration of extraction, h
F0 water-soluble	H_2O	20	2
F1 exchangeable	1 M CH_3COONH_4	20	2
F2 bound to carbonates	1 M NH_4Ac in 25% HAc, pH=5	20	2
F3 bound to Fe-Mn oxides	0.04 M $NH_2OH\cdot HCl$ in 25% HAc	80	6
F4 bound to organic matter	30% H_2O_2in 0.008 M HNO_3, pH=2	80	6
F5 acid soluble	7 M HNO_3	90	6
F6 residual	$HF+HClO_4+HCl$		

The first four fractions are represented by reactive geochemically mobile compounds that can be transformed by changing the physicochemical parameters of the environment, such as pH, Eh, salinity, organic matter content.

The last two forms are residual or geochemical-inert forms, represented by terrigenous particles, in which the radionuclides are fixed in the crystal lattice of minerals. Thus, these fractions do not represent an environmental threat to environmental objects, due to the almost impossible migration of radionuclides.

Determination of uranium isotopes. The fractions obtained during sequential extraction were transferred into 7M HNO_3 nitric acid solutions, from which an alpha spectrometric analysis was subsequently carried out. The determination of uranium isotopes was carried out according to [6-8]. Radiochemical purification was carried out by extraction with 30% tributyl phosphate solution according to the equation:

$$UO_2^{2+} + 2NO_3^- + 2TBP \leftrightarrow [UO_2(NO_3)_2 \cdot 2TBP]$$

Preparation of the counting sample was carried out by electrolysis on a steel disk using an electrolyte consisting of a mixture of a 25% solution of ammonium chloride and a saturated solution of ammonium oxalate. The resulting counting sample was measured on an Alpha-analyst high resolution alpha spectrometer (Canberra) with Genie-2000 software. The control of the chemical yield was carried out on the basis of the activity obtained previously entered strictly dosed tracer.

RESULTS AND DISCUSSION

The results of the sequential extraction of uranium isotopes according to the protocol proposed by A. Tessier are presented in table 3 and figure 2.

Table 3 – Results of alpha spectrometric measurement

Fraction	U-238, Bq/kg	U-234, Bq/kg	$^{234}U/^{238}U$	U, μg/kg
F0 water-soluble	0.50 ± 0.37	0.92 ± 0.45	1.85	40
F1 exchangeable	1.91 ± 0.71	5.2 ± 1.0	2.73	154
F2 bound to carbonates	0.96 ± 0.48	1.07 ± 0.48	1.12	78
F3 bound to Fe-Mn oxides	1.44 ± 0.55	1.32 ± 0.50	0.92	117
F4 bound to organic matter	0.30 ± 0.25	0.66 ± 0.32	2.21	24
F5 acid soluble	1.11 ± 0.30	1.0 ± 0.27	0.90	90
F6 residual	5.80 ± 0.90	6.5 ± 0.9	1.13	460

The data of table 3 shows that the content of uranium-238 and uranium-234 in water-soluble species is small and equal to 0.50±0.37 and 0.92±0.45 Bq/kg, correspondently. The exchangeable form also showed small content of uranium-238 and uranium-234, equal to 0.96±0.48 and 1.07±0.48 Bq/kg, correspondently.

The figure 2 revealed that 48% of uranium-238 is presented in residual form, and 39% of uranium-234 is presented in residual form. Uranium-238 is represented in the following order: F6 residual > F1 exchangeable > F3 bound to Fe-Mn oxides > F5 acid soluble > F2 bound to carbonates > F0 water-soluble > F4 bound to organic matter; and uranium-234 has the following order: F6 residual > F1 exchangeable > F3 bound to Fe-Mn oxides> F5 acid soluble ≈ F2 bound to carbonates ≈ F0 water-soluble> F4 bound to organic matter.

If we take into account the high total content of uranium in the waste, then uranium fixed in geochemically-labile forms can be released and migrate from the soil depending on changes in environmental conditions, such as pH, Eh, salinity, etc.

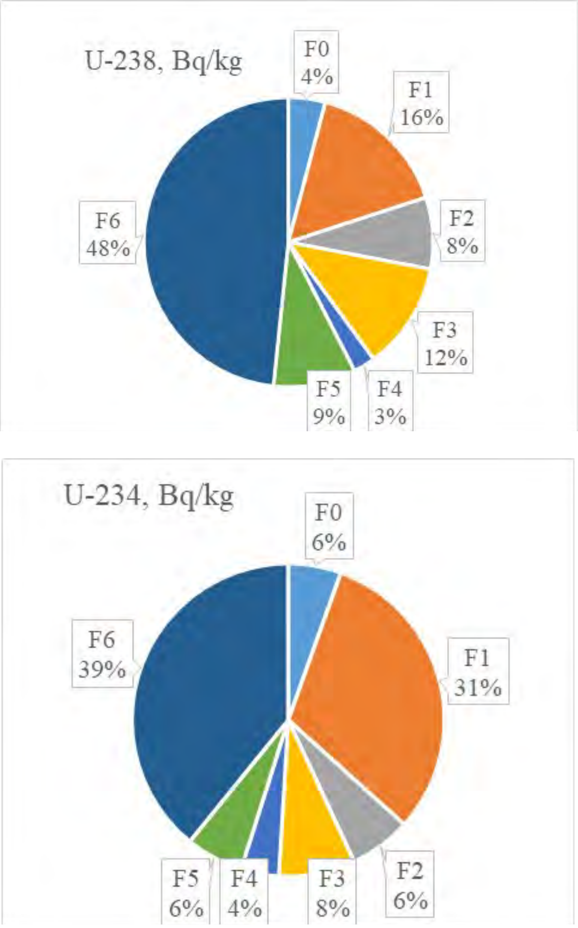

Figure 2 –Species of uranium isotopes

As about 50% of uranium isotopes is presented in mobile or potentionally mobile forms it is recommended to control the content of radionuclides in the investigated area regulary in order to prevent the potential exposure of local population.

Conclusion. The study of the sequential extraction of uranium isotopes from the waste of the Akshatau deposit, according to A. Tessier protocol, showed that uranium-238 was recorded in the following order: F6 residual > F1 exchangeable > F3 bound to Fe-Mn oxides > F5 acid soluble > F2 bound to carbonates > F0 water-soluble > F4 bound to organic matter; and uranium-234 has the following order: F6 residual > F1 exchangeable > F3 bound to Fe-Mn oxides > F5 acid soluble ≈ F2 bound to carbonates ≈ F0 water-soluble > F4 bound to organic matter.

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Резюме

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ҚАРАҒАНДЫ ОБЛЫСЫ АҚШАТАУ КЕН ОРНЫНЫҢ УРАН ИЗОТОПТАРЫНЫҢ ТАБЫЛУ ФОРМАЛАРЫН ЗЕРТТЕУ (ҚАЗАҚСТАН)

Мақалада Қарағанды облысының Ақшатау кенорнындағы уран изотоптарының табылу формалары зерттеу нәтижелері көрсетілген. Ақшатау сирек жер металлдар кен орны Жоңғар-Балқаш геосинклинасының солтүстік бөлігінде орналасқан. Түзілуі бойынша кен орны грейзенді-молибден-вольфрамды минерализациялы типке жата-ды. Элементтердің табылу формаларын анықтау ластаушы заттардың миграциялық қабілетін зерттеуде, сондай-ақ олардың биологиялық әсерін, яғни, биоаккумуляция-ны зерттеуде маңызды болып табылады. Элементтің жалпы мөлшерін білу аталған мәселелерде аз ақпарат береді.

А. Тессиер ұсынған хаттама бойынша Ақшатау кен орнының қалдықтарынан уран изотоптарын таңдамалы шаймалау әдісі арқылыанықтау, уран-238 изотопының әртүрлі табылу формаларында келесі ретте таралғандығын көрсетті: F6 қалдық > F1 ауыспалы > F3 Fe-Mn оксидтерімен байланысқан > F5 қышқылда еритін > F2 карбонаттармен байланысқан > F0 суда еритін > F4 органикалық затпен байланысқан; ал уран-234 изотопының таралу реті: F6 қалдық > F1 ауыспалы > F3 Fe-Mn оксидтерімен байланысқан > F5 қышқылда еритін ≈ F2 карбонаттармен байланысқан ≈ F0 суда еритін > F4 органикалық затпен байланысқан.

Түйін сөздер: таңдамалы шаймалау, уран изотоптары, Акшатау, табылу формалары, миграциялық қабілет, альфа-спектрометрия.

Резюме

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ИЗУЧЕНИЕ ФОРМ НАХОЖДЕНИЯ ИЗОТОПОВ УРАНА МЕСТОРОЖДЕНИЯ АКШАТАУ КАРАГАНДИНСКОЙ ОБЛАСТИ (КАЗАХСТАН)

В статье рассмотрены формы нахождения изотопов урана в Акшатауском месторождении Карагандинской области Казахстана. Акшатауское месторождение редкометалльных металлов располагается в северной части Джунгаро-Балхашской геосинклинали. По происхождению оно является грейзеновым с молибден-вольфрамовой минерализацией, генетически связанным с массивом лейкократовых гранитов пермского возраста. Формы нахождения элементов являются наиболее важными в исследованиях изучения миграционной способности загрязняющих веществ, а также их биологической способности и, следовательно, биоаккумуляции. Знание общего содержания элемента менее информативно в этих вопросах.

Изучение последовательной экстракции изотопов урана из отходов Акшатауского месторождения по протоколу А. Тессиера показало, что уран-238 представлен в различных формах нахождения в следующем порядке: F6 остаточный > F1 обменный > F3 связанный с оксидами Fe-Mn > F5кислоторастворимый > F2 связанный с карбонатами > F0 водорастворимый > F4 связанный с органическим веществом; а уран-234 имеет следующий порядок: F6 остаточный > F1 обменный > F3связанный с оксидами Fe-Mn > F5кислоторастворимый ≈ F2 связанный с карбонатами ≈ F0 водорастворимый > F4 связанный с органическим веществом.

Ключевые слова: селективное выщелачивание, изотопы урана, Акшатау, формы нахождения, миграционная способность, альфа-спектрометрия.