Estimation of Radioactivity in Dash - Salakhli Bentonite Clay: Depth and Radionuclide Migration Processes

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Abstract. This paper examines the assessment of radioactivity in the Dash-Salahly bentonite clay with a focus on depth-dependent radioactivity variations within the deposit. The study included determination of the specific effective activity of various radionuclides in soil samples collected from different depths. The results highlight that the high radioactivity of bentonite clay is primarily due to elevated levels of potassium-40 (K-40), with the highest specific activity observed at depths of 5 m, 10 m, 20 m and 25 m. Additionally, the paper compares the radioactivity levels of other radionuclides such as radium-226 (Ra-226) and thorium-234 (Th-234), noting that Ra-226 exhibits significant activity at depths of 5 m, 10 m, 15 m and 25 m, while Th-234 exhibits higher activity at depth of 20 m. These results contribute to a better understanding of radionuclide migration patterns in bentonite clay and the potential implications for environmental safety and management.

Keywords: radioactivity, radionuclides, deposit, clay rock, bentonite clay, migration, diagram.

1 Introduction

It is known that the solid upper shell of the Earth made of volcanic and sedimentary rocks is the main reservoir of natural radionuclides. In total, more than 50 radioactive isotopes with different degrees of radioactivity are present in rocks. In general, the radioactivity of rocks depends on the content of three elements in it: uranium, thorium and potassium. In addition to the radioactive elements of the uranium, actinium and thorium families, the isotopes of potassium, calcium, rubidium, zirconium, indium, tin, tellurium, lanthanum, neodymium, samarium, lutetium, tungsten, rhenium and bismuth are radioactive in nature. These isotopes are long-lived - their half-lives exceed 10^9 years.

Radioactive isotopes constitute an insignificant part of the lithosphere up to the depth of 16 km their content in % (mass) is: uranium U^{235} - $2\cdot10^{-6}$, U^{238} - $3\cdot10^{-4}$, thorium Th^{232}-$8\cdot10^{-4}$, radium Ra^{226} – 10^{-10}, actinium As^{227} – $6\cdot10^{-14}$, potassium K^{40} – $3\cdot10^{-4}$, calcium Ca^{48} – $6.4\cdot10^{-3}$ and rubidium Rb^{87} – $8.4\cdot10^{-3}$.

To determine the content of radioactive elements in rocks, the concept of radioactivity

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clark was introduced - the content of a radioactive element in the studied rock in relation to its content in the Earth's crust (in % mass):

$$Cl = \frac{Xr}{Xe.c.} \cdot 100\%$$

At present, the optimal clarks are taken for: ${}_{92}U^{238}$ – $2.1 \cdot 10^{-40}$%, ${}_{90}Th^{232}$ - $7.0 \cdot 10^{-40}$%, ${}_{19}K^{40}$ – $1.83 \cdot 10^{-40}$%.

Radioactive elements in rocks are present in more than 200 minerals, most of which contain uranium. Taking into account the prevalence of radioactive isotopes in rocks and the intensity of their decay, it can be said that U and Th with their decay products, potassium K^{40} and partly rubidium Rb^{87} can have the greatest influence on them. The other radioactive elements, due to their low abundance and long half-life, are characterized by insignificant total decay energy and cannot play a significant role in the creation of rock radioactivity [5].

The most widespread radionuclides uranium and thorium are in the magma in the dispersed state. During magma differentiation its acidic varieties are enriched with uranium and thorium. Some uranium minerals are concentrated in pegmatite, while most of them migrate in aqueous solutions and form hydrothermal deposits of uranium resin ore. Thorium minerals are mainly concentrated in pegmatite and only to a small extent participate in the formation of hydrothermal deposits due to the practical insolubility of thorium compounds. This leads to the fact that in contrast to uranium compounds, which are highly soluble in water and easily form visible deposits in sedimentary rocks, thorium minerals accumulate in placers mainly in the form of monazite. Due to the easy solubility of uranium compounds in water, uranium ore bodies are often accompanied by salt, less often by mechanical dispersion halos in surface sediments. Radium and radon formed in rocks as intermediate products of radioactive decay are partially alkalised by water. In general, basic and ultrabasic rocks are the least radioactive. In granites, granodiorites and quartz diorites, radioactive elements are much more abundant. The most radioactive elements are richest in radioactive elements in the largest, youngest in age intrusions of eruptive rocks. The highest concentrations of radioactive elements are confined to contact zones, dikes and specially to zones of hydrothermal alteration of rocks within fractures, faults, etc as well. Sedimentary rocks contain approximately the same amount of radioactive elements as eruptive rocks. The most radioactive are shales and clays, whose sorption properties are higher than those of other rocks [5, 9, 1].

The radioactivity of sedimentary rocks is associated with the presence of potassium, uranium and thorium, uranium and thorium-bearing minerals, as well as adsorbed radioactive elements. The thorium content in these rocks varies from $49 \cdot 10^{-6}$ to $3500 \cdot 10^{-6}$ kg/kg, and uranium from $12.7 \cdot 10^{-6}$ to $119 \cdot 10^{-6}$ kg/kg.

In the process of formation of ore deposits, minerals and sedimentary rocks, primary scattering halos enriched with one or another element, predominantly included in the deposit, appear around them.

The factors of migration and changes in the elemental chemical composition of the Earth's crust are continuous physical, chemical and physicochemical processes in the form of weathering, denudation and gravitational differentiation [9].

2 Problem statement

Clay rocks make up ~ 50 % of the mass of all sedimentary rocks and are found in sediments of various ages, from the Cambrian to the Holocene.

The radionuclides contained in clay rocks have a complex migration pattern and therefore the whole spectrum of migration processes in different regions of the atmosphere, hydrosphere and lithosphere must be taken into account [5-14].

Clays have a high content of U, Th and K. Relatively high radioactivity of clays and clay slates is associated with increased sorption of uranium, radium, and thorium on clay particles, as well as a relatively high content of potassium (up to 6.5%) in these rocks, which is found here not only in mineral but also in sorbed form. Significant adsorption of uranium ions is possible from natural waters, where it is present in the form of easily soluble carbonate and other compounds, for example, $Na_2UO_2(CO_3)_3$.

In modern classification systems, two features are considered: the number of particles with certain sizes in the rock, as well as the number and composition of clay (in altered rocks - mica) minerals.

Clay rocks are those in which the total content of particles < 0.005 mm and mica minerals or other layered silicates is 50% or more.

Clay rocks are a mixture of different compositions of finely dispersed minerals, which explains the variations in their chemical composition (Table 1) and the scattering of parameters characterizing rock properties [6].

Table 1. Chemical composition of fractions <0.001 mm of different clays.

Content, %	**Location, age and mineral group of clays**						
	1	**2**	**3**	**4**	**5**	**6**	**7**
SiO_2	43.93	59.34	62.91	65.04	51.21	51.40	49.78
TiO_2	1.96	0.30	следы	0.21	0.33	1.42	1.16
Al_2O_3	38.29	24.80	17.16	17.07	21.23	22.61	21.63
Fe_2O_3	1.05	2.26	2.88	3.39	4.90	7.91	6.53
FeO	Нет	0.33	0.22	0.21	2.94	0.76	1.89
MnO	Нет	-	следы	-	-	-	0.05
CaO	0.28	2.14	0.74	0.83	1.29	0.48	1.53
MgO	0.15	3.85	5.41	3.53	4.24	3.07	4.15
K_2O	0.16	0.20	1.54	0.15	6.23	5.78	6.15
Na_2O	0.38	0.19	1.53	2.37	0.33	0.64	0.24
$\pm H_2O$	-	-	-	5.17	4.36	5.74	5.90
l.o.i.	13.53	6.64	7.36	6.11	7.23	5.96	6.89

Note: ± H_2O – water loss to temperature 350°C; l.o.i. – loss on ignition.

1 - Novgorod region, Lower Carboniferous, dry clay (kaolinite argillite);
2 - Northern Urals, Mesozoic, montmorillonite clay;
3 - Uzbekistan, Alai Stage (Eocene), montmorillonite clay;
4 - Azerbaijan, Paleogene, montmorillonite clay (bentonite);
5 - Leningrad Region, Lower Cambrian, hydrous mica clay;
6 - Leningrad Oblast, Middle Cambrian, hydrous clay;
7 - Leningrad Region, Upper Devonian, hydrous clay.

The ability to absorb and retain various substances and individual elements in its volume is the most important property of clay rocks used for underground isolation of radioactive waste (RW) [7, 10]. As polymineral natural formations, clays are mixed-porous adsorbents having all kinds of pores whose diameter (2000-15Å) is commensurate with the size of adsorbed molecules.

According to structural and mineralogical features, the following most common groups are distinguished among clay minerals:

– kaolinite group;
– montmorillonite group;
– the mixed group of illite and hydrous micaceous minerals.

Montmorillonite is formed mainly during the weathering of the main eruptive rocks in an alkaline environment. Many montmorillonite (bentonite) clays are the product of decomposition of volcanic ashes deposited in marine basins. In terms of composition, the products of volcanic activity correspond to medium-acid eruptive rocks: trachytes, andesites, etc. (65-52 % SiO_2). (65-52 % SiO_2).

Montmorillonite (bentonite, smectite) clays are successfully used for creation of sorption-hydroisolation barriers for isolation of radioactive wastes.

Dash-Salakhli bentonite clay deposit is one of the highest quality natural sodium deposits in the world and represents a single horizontally lying stratum with no interlayers of waste rocks inside. The deposit belongs to the sedimentary type formed in lacustrine continental conditions (Fig. 1) [9, 14, 15].

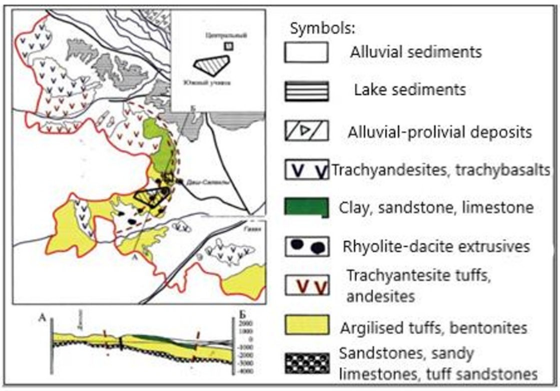

Fig. 1. Geological scheme of the Dash-Salakhli field structure.

The deposit is represented by montmorillonite and hydrosludis to montmorillonite clays. The extracted bentonitic clays of Dash-Salakhli birthplace contain more than 85 % of montmorillonite, in the volume complex of which sodium and magnesium cations predominate. Physical and chemical properties of Dash-Salakhli bentonite clay have been studied to a sufficient extent. However, the study of radioactive properties of this clay remains among the poorly studied issues. Taking into account the wide use of bentonite clay in different fields of industry, undoubtedly, it is necessary to take into account its radiation properties in order to ensure the safety of working personnel and consumers of finished products. Proceeding from the above stated, the purpose was set to estimate radioactivity of Dash-Salakhli bentonite clay at the depth of the deposit.

As it is known, migration of radionuclides and their compounds occurs due to endogenous, exogenous, metamorphic and other processes accompanied by geochemical differentiation of migrating components composition. A detailed analysis of natural systems of migrant movement (differentiation) in the systems of dispersion halos allows us to scientifically justify the modelling of complex migration processes. Natural analogues, primarily deposits of radioactive elements [1, 5-9, 12], are used to assess the development in space and time of scattering halos of individual radionuclides.

Bentonite clay is a strong insulating effective barrier medium that limits migration processes and has the ability to retain radionuclides.

The literature [14] classifies sedimentary materials according to the degree of radioactivity in the following sequence:

1. Low activity (up to 3.65 Bq/kg) - quartz, calcite, dolomite, siderite, anhydrite, gypsum, rock salt.
2. Medium activity (3.65; 36.5 Bq/kg) - limonite, barite, magnetite, tourmaline, corundum, garnet, hornblende.
3. Elevated activity (36.5; 365 Bq/kg) - mica, clays, feldspars, potassium salts, apatite, glauconite, tarapeli, kaolin, hydrous mica, clay bentonite, obsidian, sylvin.

4. Extremely high activity (>365 Bq/kg) - zircon, monazite, orthite.

Currently, a large number of scientific articles have been published, which reflect the processes of formation, migration and deposition of natural and artificial radionuclides in the biosphere. However, due to the complexity and diversity of these processes, their qualitative description is not possible in all cases. For a comprehensive understanding of these processes, it is necessary to take into account the physical, chemical, geophysical, geochemical, physicochemical and biochemical properties of radionuclides, as well as the regularities of their migration processes in different regions of the atmosphere, hydrosphere and lithosphere [9, 15].

3 Methods of determination and experimental methodology

The main methods of studying the natural radioactivity of the Earth's crust and searching for accumulations of radioactive minerals are radiometric methods, primarily various modifications of integral differential spectrometric gamma-ray spectroscopy [5, 9]. The gamma spectroscopic method is based on the difference in the spectral composition of gamma radiation of uranium and thorium families, as well as potassium.

The purpose of this stage of research is to determine the specific effective activity of such natural radionuclides as radium, thorium, potassium depending on different depths of bentonite clay layers. For radionuclide analysis 5 sample materials from Dash-Salakhli bentonite clay were taken. A trend map constructed by the author of [12] was used, which made it possible to follow the regular and random changes in the parameters of rock sediments in the Dash-Salakhli deposit during the sampling process. Studies of radionuclide composition of bentonite clay taken from different (5, 10, 15, 20, 25 m) depths of the deposit were carried out in the Institute of "Radiation Problems'" Azerbaijan National Academy of Sciences. Determination of radionuclide composition was carried out in γ-spectrometric system by available Ge detector with high selectivity (production of "CANBERRA" company on the basis of standard methods EPA901.1 and ASTMC140204 (2009). Samples were placed in cylindrically shaped plastic dishes, covered with a lid and then coated with a thin layer of paraffin to create an airtight seal. Prior to analysis, a standard source spectrum consisting of Na^{22}, Eu^{22} isotopes gave quality assurance when closed and the camera spectrum travelled to control the quality procedures. Samples were placed in a special lead structure and spectra were taken within 24 hours. Using the "ISOCS LabSOCS" provision programme, the geometric efficiency of the dishes was calculated. Using the 'Genie-2000' software programme, radionuclide identification and activity estimation was carried out. At this time, γ -lines 186.1 keV; Ra^{226}, 351.9 keV; Pb^{214}, 609.32 keV, 1120.28 keV and 1764.49 keV; Bi^{214}, 338.40 keV were used; Ac^{228}, 583.14 keV and 2614.5 keV; Tl^{208}, 911.07 keV, 964.60 keV and 968.90 keV; Ac^{228}, 1460.8 keV; K^{40}, 661.6 keV; Cs^{137}, 604.7 keV; Cs^{134} and 1173 keV Co^{60}. Only decay products of K^{40}, U^{238}, Th^{232} radionuclides of natural origin were observed in the samples.

4 Experimental results and radioactivity assessment

The results of the analysis of radionuclide composition of Dash-Salakhli bentonite clay are given in Table 2 [2]. As can be seen from the table, the obtained radioactivity values for the 4th and 5th samples taken from 20 and 25 m depth, respectively, the radioactivity values (376.3 Bq/kg) and (369.1 Bq/kg) are very different from the radioactivity values (36.5-365 Bq/kg) established according to the classification of sedimentary materials according to the degree of radioactivity (increased activity). Thus, the radioactivity values of these samples correspond to very high activity according to the sediment radioactivity classification. This suggests that clay bentonite cannot have such a high activity.

Such a contradiction with the literature data [14] leads to the idea that the reason should be sought in the radionuclide composition of these samples. In fact, if we pay attention to the radionuclide composition of the above-mentioned samples, we will see that in the 4th sample very high activity is obtained at the expense of K^{40} (163.8 Bq/kg), Ra^{226} (61.43), Th^{234} (<56.76 Bq/kg) and in the 5th sample - at the expense of K^{40} (136.9 Bq/kg), Pb212 (40.50 Bq/kg), Th^{232} (70.56 Bq/kg). In our opinion, this pattern is more likely to be associated with complex endogenous and exogenous processes occurring in Dash-Salakhli bentonite clay deposit.

Table 2. Radionuclide composition of Dash-Salakhli bentonite clay.

Bq/kg	1	2	3	4	5
K^{40}	62.14	91.7	30.24	163.8	136.9
Co^{60}	<1.8	<1.9	<2.07	<1.9	<1.7
Cs^{134}	<2.3	<2.5	<2.5	<2.4	<2.2
Cs^{137}	<2.1	<2.3	<2.2	<2.1	<2.1
Ti^{208}	14.74	14.77	11.51	11.46	12.63
Bi^{210}	<2.4	<2.6	<2.5	<2.4	<2.2
Bi^{212}	40.41	32.23	29.05	19.08	29.27
Pb^{212}	48.12	48.69	37.08	34.26	40.50
Bi^{214}	<5.4	27.17	26.11	22.82	17.93
Pb^{214}	14.38	30.61	27.59	26.46	18.71
Ra^{226}	46.09	26.82	25.61	61.43	18.01
Ac^{228}	42.50	42.60	37.59	33.49	39.17
Th^{234}	<56.6	<60.61	<56.76	<56.66	<70.56
U^{235}	2.63	5.41	4.79	3.5	3.42
Total	276	291.2	204.1	376.3	369.1

By analyzing and comparing tabular data (Table 2) on the activity of the studied radionuclides, a diagram (Fig.2) showing the dependence of radioactivity of elements on the depth of the place where the samples were taken was constructed. As can be seen from this figure, at depths of 5; 10; 20; 25m the highest specific activity is K^{40}, and at depths of 10 and 25 m - Th^{234}. At depths of 5, 10, 15, 25m the specific activity of Ra^{226} compared to K^{40} and Th^{234} is significantly low.

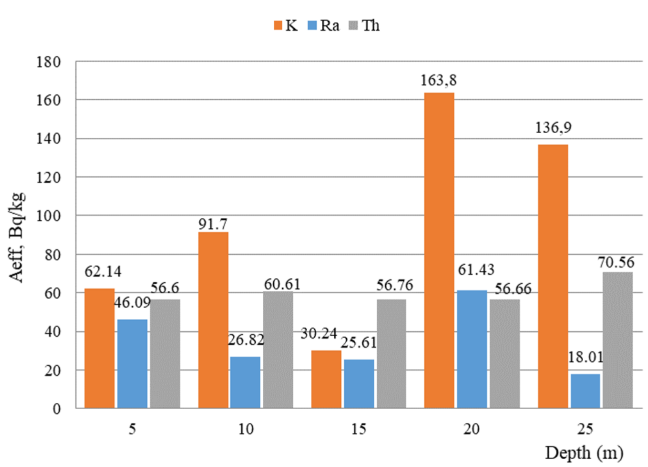

Fig. 2. Diagram of specific effective activity of radionuclides by depth of Dash-Salakhli bentonite clay deposit, (Bq/kg).

Thus, conducting a comparative analysis of the diagram (Fig. 3) on specific effective activity (in percentage) of radium, thorium and potassium in bentonite clay, the following conclusions can be drawn:

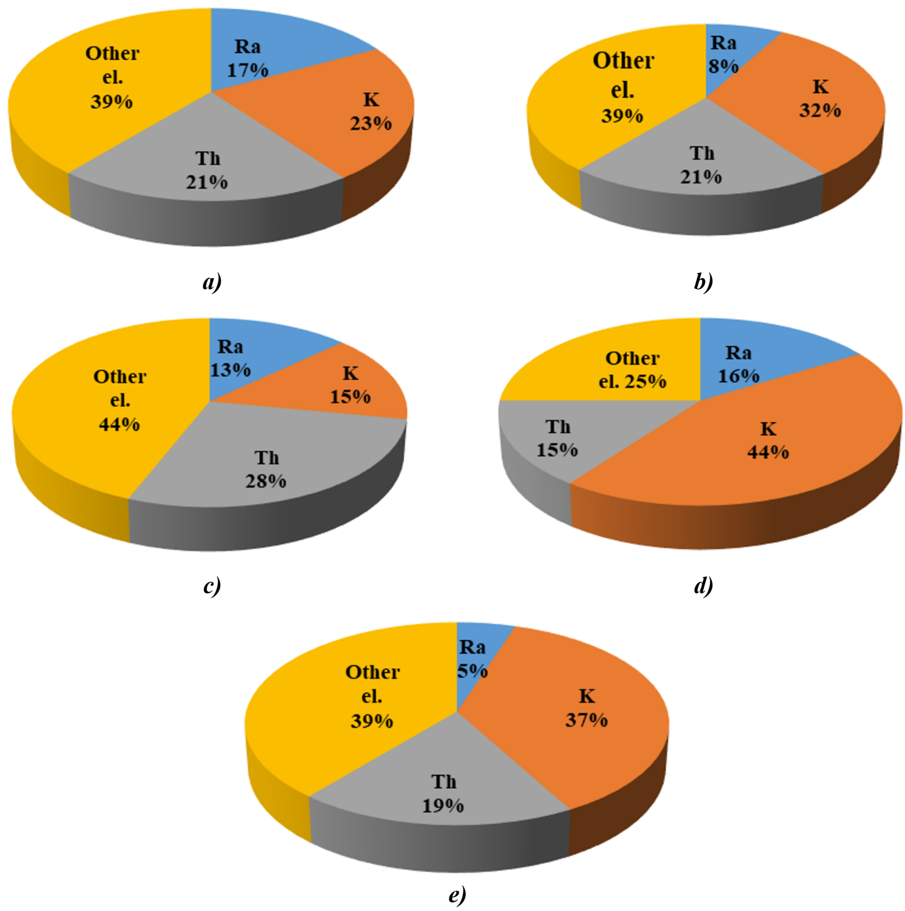

Fig. 3. Comparison diagram of specific effective activity (in percentage) of radium, thorium and potassium in bentonite clay: a) at a depth of 5m, b) at a depth of 10m, c) at a depth of 15m, d) at a depth of 20m, e) at a depth of 25m.

Radioactivity at a depth of 5m is due to the highest potassium activity (23 %). Thorium also makes a significant contribution (21 %) to the total radioactivity. Most of the total clay radioactivity at 10m depth is due to potassium (32 %) and thorium (21 %), with a slightly minor contribution from radium (8 %). Radioactivity at 15 m depth is due to thorium (28 %) being the most active. Radium (8 %) and potassium (15 %) also contribute to the total radioactivity. At depths of 20-25 m, potassium radioactivity dominates (44 and 37 %)

The charts were drawn up based on the data obtained (in %) presented in Table 2. Since this table contains numerical activity values for all elements as well as for each element separately, it is possible to calculate the percentage activity of any radionuclide relative to the total cumulative radioactivity, which was done for the more significant elements in this work.

5 Conclusion

On the basis of gamma (γ) - spectrometric analysis of the studied samples of bentonite clay of Dash-Salakhli deposit it was revealed that the 4th and 5th samples are relatively anomalous in terms of radioactivity level. Their level of radioactivity, which significantly exceeds the level of natural radiation background, poses a certain radiological hazard on the surface of the said deposit, where the samples were taken.

As a result of the analysis and comparison of tabular (Table 2) data on the activity of the studied radionuclides, a diagram (Fig. 2) was constructed showing the dependence of the radioactivity of elements on the depth of occurrence. It was revealed that at the depths of 5; 10; 20; 25m comparatively the greatest specific activity has K^{40}, at the depths of 10 and 25 m Th^{234}. The specific activity of Ra^{226} in comparison with K^{40} and Th^{234} is considerably low at these depths (Fig. 3).

It was found that the radioactivity at a depth of 5m is due to the highest activity of potassium (23%), thorium (21%), at a depth of 10m potassium (32%) and thorium (21%) and somewhat insignificant in comparison with them the contribution of radium (8%). Radioactivity at 15m depth is due to the highest activity of thorium (28%). At depths of 20-25 m, potassium radioactivity prevails respectively (44 and 37%)

Diagrams were made on the basis of the obtained data (in %) according to Table 2. The diagram shows our calculated values of specific activity of more significant radionuclides relative to the total cumulative radioactivity.

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