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Weathering Products of Basic Rocks as Sorptive Materials of Natural Radionuclides

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MATERIALS OF NATURAL RADIONUCLIDES**

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WEATHERING PRODUCTS OF BASIC ROCKS AS SORPTIVE MATERIALS OF NATURAL RADIONUCLIDES

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The principal requirements for employing natural minerals as buffer and backfill material in high-level waste (HLW) repositories are high sorptive properties, low water permeability, relatively high thermal conductivity, and thermostability. The major task of the buffer is to prevent the penetration of radionuclides into groundwater.

In most waste-isolation technologies montmorillonite with a mixture of quartz sand is considered for use as a buffer material. Montmorillonite's advantages are its low water permeability and high sorptive characteristics relative to Cs and Sr. At the same time, the results of radiogeochemical investigations indicate that montmorillonite is not an optimum sorptive barrier. Montmorillonite is less effective than many other abundant minerals, especially those formed in the weathering processes of basic igneous rocks.

HLW contains a wide range of radionuclides that are characterized by various geochemical properties. Therefore, one mineral cannot provide sorption for all radionuclides. Some minerals can restrain radionuclides thanks to their cation exchange capability; others retard radionuclides because of their reductive properties or large specific surfaces. Along with montmorillonite, the weathering products of basic rocks also contain various mixed-layered minerals; hydromicas; oxides and hydroxides of Fe, Mn, and Ti; and many others. All secondary minerals that are formed at the expense of olivine, pyroxene, hornblende, and biotite have high sorptive capacity. Effective buffer materials have particularly great importance for Russia, where the existence of a great volume of HLW and a very difficult economic situation do not allow the use of expensive engineered barriers. The most efficient method of HLW disposal consists in the maximum use of natural inexpensive minerals for engineered barriers and the inherent protective capacities of host rocks.

Radiogeological prerequisites for selection of sorptive natural materials

Wide application of the fission-track radiography method for studying uranium distribution in rocks and minerals allowed us to accumulate substantial information on uranium behavior in various geological processes. The behavior of uranium under granitization, regional and contact metamorphism, magmatic melt crystallization, and hydrothermal-metasomatic and hypogene processes was studied [Gavshin et al., 1975; Eliseeva, Omelianenko, 1976; Omelianenko et al., 1983]. The following results bearing on the problem of interest were obtained: (1) all geological processes are accompanied by

supply, loss, or redistribution of uranium; (2) in more than 95% of rocks uranium is fixed in discrete minerals, while the other minerals contain practically no uranium; (3) in magmatic and high-temperature hydrothermal-metasomatic rocks uranium concentrates either in uranium minerals or, in its isomorphic state, enters into the internal crystal framework of accessory minerals; (4) as the temperature of geological processes falls, uranium is increasingly observed in the sorptive state; (5) all geological processes involving the formation of secondary minerals containing titanium and iron are always accompanied by uranium accumulation in these minerals; (6) the greatest amounts of such minerals form in the weathering processes of basic rocks; (7) consequently, the material from weathered basic rocks is characterized by high sorptive properties for uranium.

It is important to emphasize that uranium sorption takes place both in reductive and in oxidative conditions; thus uranium accumulation is not limited to its reductive state.

One can conclude that the other radionuclides of the transuranic group will also be intensely sorbed by the residuum of weathered basic rocks. But to verify such an assumption the properties of buffer and backfill material must be characterized for their high sorptive capacities of both Sr and Cs as well as U.

We conducted a study of Cs and Sr sorption by natural minerals and their mixtures under static conditions. To provide homogeneous samples, each specimen was broken into pieces measuring less than 0.5 mm. A 0.3-gram sample was saturated by 50 milliliters of SrCl_2 or CsCl solution. The saturated sample was agitated by periodic shaking for 150 hours. This time was sufficient to attain chemical equilibrium between fluid and solid phases. The resulting solution was then centrifuged and analyzed for Sr or Cs. The concentration of these elements in the solid phase was calculated by the difference between the initial and the final Sr or Cs concentration in the solutions. The distribution coefficients (K_d) were determined by the concentration ratio of Sr and Cs in solid and liquid phases.

The subjects of inquiry

Weathered basic rocks from three regions were studied by the authors: (1) dunites of the Kovdor massif (Kolsky peninsula); (2) basalts of the Sarimbet tin deposit (Kazakhstan, Kokchetavsky region); and (3) basalt-porphyrates of the "Mayak" district (South Ural region). In all cases, the thickness of weathered rock profiles varies from less than a meter to several dozen meters. Samples were collected mainly at sites that are characterized by a maximum thickness of weathered rocks. The resulting product of weathering is a medium that consists completely of secondary minerals.

The most time-consuming procedures were a definition of average mineral composition as well as different monomineral fractions. If the extraction of a specific mineral was impossible, the sorptive properties of fractions containing different amounts of this mineral were determined. Thus a contribution of each mineral to the sorptive capacity of weathered rocks was estimated.

The identification of minerals was carried out in the x-ray diffraction laboratory of the Geological Institute and in the laboratory of electron microscopy of the Institute of Ore Deposits, Russian Academy of Science. A.K. Dritz, A.I. Gorshkov, and their collaborators participated in the study.

Sorptive properties for Sr and Cs in weathered basic rocks

Only the upper part of the weathered profile on Kovdor massif dunites was investigated. It consists mainly of lizardite, vermiculite, and stevensite. Oxides and hydroxides of Fe, Ti, and Mn are present as an admixture. In the lower part of the weathered profile the rocks contain primary minerals partly oxidized and replaced by secondary minerals. The only primary mineral of dunite characterized by high sorptive properties is phlogopite (Table 1). The combination vermiculite + lizardite + 10% stevensite has by far the highest sorptive properties for Cs, and vermiculite has the highest sorption for Sr.

Table 1. Sorptive parameters of weathered dunites Kovdor massif.

Mineral composition	Concentration in starting solution n·10 ⁻⁴ %		% of element sorbed by solid phase		Kd	
	Sr	Cs	Sr	Cs	Sr	Cs
Weathered dunite	15.1	50.5	56	32	209	78
	-	10.1	-	49	-	73
Lizardite	44.2	32.8	26	37	60	77
	15.1	10.1	42	51	123	177
	2.5	-	65	-	307	-
Vermiculite	184	107.5	26	98.8	57	12000
+lizardite+	44.2	53.5	39	97.6	107	6700
10% stevensite	2.5	50.5	50	98.3	162	9735
Vermiculite	15.1	50.5	75	86	496	986
	2.5	10.1	81	79	701	627
Phlogopite	15.1	50.5	81	56	732	212
	2.5	10.1	93	87	2150	1100

The basic rocks of the Sarimbet tin deposit are primarily gabbro-diabase. Among weathered rocks three zones are distinguished. The upper zone consists of kaolinite with a montmorillonite admixture. In the middle zone kaolinite and montmorillonite prevail. In the lower zone montmorillonite, kaolinite, and mixed-layered chlorite-montmorillonite are predominant (Table 2). Oxides and hydroxides of Fe, Ti, and Mn in all zones and chlorite in the middle and lower zones are present as an admixture. The data in Table 2 indicate that the montmorillonite-kaolinite zone is the most sorptive.

Table 2. Sorptive parameters of weathered gabbro-diabases of Sarimbet tin deposit.

Mineral composition	Concentration in starting solution		% of element sorbed by solid phase		Kd	
	Sr	Cs	Sr	Cs	Sr	Cs
Kaolinite +montmorillonite	5.8	10.0	60	51	257	177
	15.4	49.5	52	34	183	87
Montmorillonite +kaolinite	5.8	10.0	83	85	781	983
	15.4	49.5	77	79	556	619
Montmorillonite+kaolinite+chlorite-montmorillonite	5.8	10	74	75	500	514
	15.4	49.5	68	60	352	246

The study of weathered rocks of the "Mayak" region is very important since the search for effective sorptive material here is a particularly urgent task.

Volcanic rocks of the "Mayak" region consist of moderately metamorphosed basalts, andesite-basalts, andesites, welded tuffs, scoriaceous lavas, tuffs, and tuff breccias moderately metamorphosed to green schist facies. Labradorite and pyroxene are partly or completely replaced by albite-actinolite-epidote-chlorite-calcite. The average chemical composition all of these rocks in weight % is: SiO₂—50.96; TiO₂—0.84; Al₂O₃—15.35; Fe₂O₃—5.59; FeO—4.84; MnO—0.15; MgO—8.89; CaO—9.88; Na₂O—2.99; K₂O—0.51. The rocks are composed of variable quantities of pyroxene, plagioclase, amphibole, epidote, chlorite, and carbonate. Pyrite, leucosene, zeolite, and quartz are present as admixtures.

The thickness of weathered volcanic rocks varies from less than a meter to 120 meters. The weathered part of the fractured metavolcanic rocks is the basic aquifer that determines the regional hydrological conditions in the volcanites.

Three zones in the weathering profile can be distinguished: clayey, transitional, and a zone of disintegration. The clayey zone consists of two parts: kaolinite prevails in the upper part and montmorillonite in the lower one. Mixed-layered chlorite-vermiculite is

present in all zones of the weathered profile. In the transitional zone, along with supergene minerals, fragments of unaltered volcanites are present. The supergene mineral content in this zone varies from 5% to 20%. The zone of disintegration is intensively fractured and composed of fragmental volcanites that contain less than 5% supergene minerals. Besides the minerals shown in Table 3, an admixture of oxides and hydroxides of Fe, Ti, and Mn is present in every zone. The quantity of supergene minerals depends on the degree of schistosity and structure of volcanites. The intensity of supergene processes in tuffs is in general much higher than in lavas and scoriaceous lavas.

Table 3. Sorptive parameters of weathered volcanites from the "Mayak" region.

Zones	Mineral composition		Concentration in starting solution		% of element sorbed by solid phase		Kd	
			$n \cdot 10^{-4} \%$					
	Chief	Minor	Sr	Cs	Sr	Cs	Sr	Cs
Clay	Kaolinite chlorite-vermiculite	Chlorite- mica, montmorillonite	5.68	14	95	95	2989	2987
			15	56	89	95	1396	3052
Clay	Chlorite-vermiculite, montmorillonite	Kaolinite, chlorite- mica	5.68	14	94	97	2792	4695
			15	56	87	98	1115	7013
Transi- tional	Chlorite-vermiculite, chlorite- mica, montmorillonite	Chlorite-montmorillonite, kaolinite	5.68	14	93	96	2200	3856
			15	56	87	97	1115	6055
Disinte- grated	Chlorite, chlorite-montmorillonite	Chlorite-vermiculite, montmorillonite	5.68	14	91	92	1727	1955
			15	56	80	83	681	826
Clayey residuum from well 5-90	-	-	3.08	14.5	97	99.1	5474	17778
			5.50	56.0	73	99.6	457	39048

It should be noted that the values of Kd for different samples of weathered volcanites vary over a wide range, and at present time we cannot explain the reasons for these variations. The quantitative mineral compositions of many samples have not yet been determined; that work is in progress. Nevertheless, we can conclude that the sorptive properties of weathered volcanites are rather high and in some places very high.

For comparison, commercial sorptive materials were also investigated (Table 4).

Table 4. Sorptive parameters of some commercial sorptive materials.

Mineral sorptive materials	Fraction dimension mm	Concentration in starting solution $n \cdot 10^{-4} \%$		% element sorbed by solid phase		Kd	
		Sr	Cs	Sr	Cs	Sr	Cs
Glaucinite, Karachaevskoe deposit	-0.25 -	5.68	14.	87	76	1148	540
	+0.1	15	56.	79	63	627	289
	<0.1	5.68	14.5	86	78	988	589
		15	56	79	65	627	312
Saponite, Tashky deposit	-0.25 -	5.68	14	88	79	1186	611
	+0.1	26.2	56	83	74	804	477
	<0.1	3.08	10	84	81	860	688
		26.2	44	79	77	627	552
Clinoptilolite, Sokimitskoe deposit	-0.25 -	3.08	14.5	97	99.3	6250	16500
	+0.1	26.2	56	92	98.9	2772	15390
	<0.1	3.08	14.5	97	99.3	6250	24000
		26.2	56	93	98.8	2372	14193
Palygorskite, Cherkasskoe deposit	-0.25 -	5.68	14.5	82	89	780	1339
	+0.1	15	56	73	71	443	410
Bentonite, Cherkasskoe deposit	-0.25 -	5.8	10.0	88	88	1167	1222
	+0.1	15.4	49.5	86	84	1027	865

The data show that the sorptive parameters of weathering products of basic rocks for Sr and Cs are as a whole equivalent to industrial sorptive materials. Earlier work indicates that the sorptive capacities for uranium of weathered basic rocks are high enough for these rocks to be considered dependable engineered barriers. As for the other radionuclides of the transuranic group, it is highly likely they will also be successfully sorbed by weathered basic rocks, at least as well as by montmorillonite. This line of inquiry is very urgent.

Conclusions

1. Sorptive properties of weathered dunites, gabbro-diabases, and basic volcanites for Sr and Cs were studied. The results show that the sorptive capacities of weathered basic rocks are equivalent or, in some cases, superior to industrial sorptive materials.
2. Results of the uranium distribution study by fission-track radiography suggests that material from weathered basic rocks is characterized by high sorptive properties for uranium. One can assume that the other radionuclides of the transuranic group will likewise be intensely sorbed by the residuum of weathered basic rocks. The study to confirm this assumption is one of the most important areas in current research.

3. Discovery of an effective sorptive material that can be used for rehabilitation of polluted water and nuclear waste disposal is of particular importance for the "Mayak" region, where this problem is very urgent.

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