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Geoecological Approach to the Choice of Mineral-Like Matrices as Radionuclide Containers for Permanent Burial in Granitoids

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Abstract

By the example of the Niznekansk granitoid mountain range as a prospective platform for the burial of high-level active waste (HAW), the application of the geoecological approach to the choice of matrices for permanent HAW disposal in mountain ranges has allowed one to choose the minerals specific for granitoids those are capable to incorporate isomorphically some fractions of radionuclides. The matrix materials similar to the structural types of skeletal fieldspars and feldspathoids (for the burial of ^{135}Cs, ^{137}Cs and ^{90}Sr), as well as zircon, monazite, kosnarite (NZP), apatite, sphen (for the incorporation of actinoids and lanthanoids), suit the principle of the physicochemical conformity between the matrix and the host granitoid rocks, which could allow one to provide the geochemical balance under the permanent burial of HAW within a granitoid mountain range. The potentiality is demonstrated for obtaining such mineral-like materials with a predicted structural type using prospective multifunctional porous materials on the basis of an available raw material such as hollow aluminosilicate micro-spheres (so called cenospheres) from volatile ashes formed due to the incineration of power station coal.

Key words: mineral-like matrices, cenospheres, radioactive waste products, granitoids

INTRODUCTION

The contemporary approach to the conditioning of radioactive effluents – liquid radioactive waste products (LRW) – implies minimizing the volumes of the LRW formed within the closed nuclear fuel cycle at various stages of radiochemical processing of spent fuel (SF) as well as the liquidation of vast volumes of the already accumulated LRW formed during the realization of military programs, the process of electricity generation at atomic power plants (APP), the operation of vehicle nuclear power systems, the use of radioactive substances and the sources of ionizing radiation.

By the beginning of 2003 there was more than 467 million m^3 LRW with the activity almost 2 billion Ci ($6.87 \cdot 10^{19}$ Bq) and 72 million tons of solid radioactive waste products (SRW) with the activity of 0.3 billion Ci ($1.03 \cdot 10^{19}$ Bq) [1] in Russia at the enterprises of the Russian nuclear complex. Additionally, there is 5 million m^3 LRW with the activity of 77 million Ci and 1 million ton SRW with the activity of 2.4 million Ci [2] formed every year. Thus, the LRW include 87 % of the total activity of radioactive waste products stored, and 97 % of the activity of RW formed annually [1]. The liquid high-level active waste products (HAW) are of the greatest radiation hazard since they exhibit the greatest specific radiotoxicity and contain long-living radionuclides. Thus for today the urgent problem of atomic power engineering and all the nuclear complex as a whole consists in the liquidation of great volumes of LRW accumulated, first of all HAW providing their reliable environmentally safe isolation. One of the solutions of this problem implies the reduction of their radiation hazard, fractionating and transforming the most dangerous LRW components to yield the solid with the incorporation of radionuclides into radiation resistant, chemically and mechanically stable matrices, then the storage and permanent underground burial within geological depositories. According to the IAEA declaration, the use of such depositories is a unique comprehensible solution for the completion of the nuclear fuel cycle, which is achievable in the nearest future [3].

Crystalline rocks (granites, basalts), clay and salt domes are considered to be a geological environment for the burial of HAW at the majority of the states those are the IAEA members [4]. The burial is carried out with the observance of the multibarrier burial principle, *i. e.* the isolation of radionuclides is provided by the combination of engineering barriers (matrix, packing of waste products, engineering equipment, and storehouse) and natural barriers (geological environment such as rock, salt, clay).

The matrix materials such as borosilicate and aluminium phosphate glasses being used today for industrial neutralization of radionuclides, under the conditions of burial underground disposal in within the earth's crust are thermodynamically unstable being in the course of time and/or under hydrothermal conditions undergone devitrification, which worsens, as a rule, chemical stability and mechanical durability of the material.

Searching for materials those represent an alternative to glass for in the immobilization of radioactive waste (RW) began since 1950ths when L. P. Hatch [5] has suggested to apply for these purposes mineral phases whose stability remains intact under natural conditions for a long time. Such a geochemical approach has allowed Ringwood *et al.* to develop a series of polyphase ceramics (so-called synrock) those exhibit a higher stability as compared to glasses [6] due to the incorporation of radionuclides into crystal phases (the analogues of stable natural minerals), such as zirconolite $CaZrTi_2O_7$, hollandite $Ba_xCa_y(Ti^{3+},Al^{3+})_{2x+y}(Ti^{4+})_{8-2x-y}O_{16}$, perovskite $CaTiO_3$ and titanium oxides, such as mainly rutile TiO_2 [7]. However, despite of plausible physicochemical and mechanical properties of the synrock, a high cost of its manufacture as well as of source materials, a relative complexity of the production process flowsheet to a considerable extent constrain a wide application of this material for radionuclides to immobilize.

In order to immobilize the most problem radionuclides (such as heat-generating Cs and Sr and long-living actinoids) the search and development of various matrix materials is actively conducted all over the world [6, 8–12]. The development of energy saving methods for obtaining various matrix materials with the structures similar to the structures of stable minerals whose crystal lattices are capable to incorporate radionuclides on the basis of isomorphic substitution, is of particular importance. In this case one should take into account the mineral composition of host rocks of the geological platforms chosen for HAW burial place, since each of these matrix materials under particular geological conditions could exhibit certain advantages and disadvantages. The geoecological approach allows one to minimize adverse consequences of a burial, when for a geological platform assumed for a burial place such mineral-like materials are developed those are the analogues of stable natural minerals inherent in the geological formations type under consideration, whose crystal structures could incorporate radionuclides due to isomorphic substitution. Such approach allows the system to conserve geochemical equilibrium between a matrix material and the host rocks under the conditions of HAW burial, which could provide the chemical stability of matrices within a long period of time and, hence, the environmental safety of the HAW burial place.

The present review within the framework of the geoecological approach deals with the consideration of criteria for the choice of stable minerals whose structures could be used in order to immobilize various radionuclides with the purpose of permanent HAW burial within the strata of granitoid rocks A potentiality is demonstrated for obtaining such mineral-like materials with a predicted structural type using a cheap and accessible raw material such as hollow aluminium silicate microspheres (so-called cenospheres) produced as a volatile ash by-product of coal combustion at thermal power plants.

TABLE 1

Compositions of liquid highly active waste products, g/L [6, 15]

Component	Savannah River (the USA)	Hanford (the USA)	West Valley (the USA)	Idaho Falls (the USA)	Tokai (Japan)	Lanchow (China)	Sallugia (Italy)	Sicral 1 (France)	La Hague (France)	Magnox (Great Britain)	THORP (Great Britain)	HEWC (Belgium)	HAWC-WAK (Germany)	WIP (India)
H^+	–	–	–	–	2.5 M	1.5 M	1.3 M	–	–	–	–	–	–	–
Al	7.7	1.5	3.9	4.2	–	4.5	20.4	32.5	–	26.0	–	44.0	0.2	–
Na	5.9	4.1	10.3	3.1	44.5	31.0	–	20.5	–	–	0.1	1.9	16.0	6.6
K	0.3	–	0.1	0.9	–	0.6	–	–	–	–	–	–	0.4	0.2
Mg	0.2	–	0.3	–	–	–	–	4.0	–	30.0	–	–	0.2	–
Fe	29.7	6.1	20.6	–	8.4	13.5	0.6	16.0	20.0	13.0	4.0	1.3	5.2	0.5
Ni	2.8	0.6	0.5	–	2.2	2.9	–	1.5	3.2	1.4	–	–	1.2	0.1
Cr	0.3	0.1	0.3	–	2.2	1.2	–	1.5	3.4	1.6	–	0.1	1.3	0.1
Mo	0.2	0.2	–	–	–	0.7	–	–	–	10.8	18.3	–	–	–
Zr	0.6	3.4	0.4	11.4	–	0.7	–	–	–	11.8	20.1	–	–	–
Hg	0.8	–	–	–	–	–	1.0	–	–	–	–	2.8	–	–
Cl	0.9	0.1	–	–	–	–	–	–	–	–	–	–	–	–
SO_4	0.8	0.2	1.1	2.6	–	4.8	0.6	–	–	–	–	3.2	–	0.5 M
NO_3	4.2	2.8	20.6	12.5	–	–	–	–	–	11.0 M	–	–	–	4.1 M
FP	<3.0	<2.5	<1.5	<1.0	49.0	2.7	–	24.5	87.0	–	–	0.5	40.5	1.1
TUE	<0.2	<0.1	<0.2	<0.1	12.6	17.9	–	3.0	5.1	2.0	4.5	0.1	6.9	7.6

Note. FP – fission products; TUE – transuranium elements; M – molar concentration; THORP – Thermal Oxide Reprocessing Plant; HEWC – Highly Enriched Waste Concentrate; HAWC – Highly Active Waste Concentrate; WIP – Waste Immobilization Plant.

BASIC APPROACHES TO PERMANENT BURIAL OF HIGH-LEVEL ACTIVE WASTE

The major factors determining the duration and method required for reliable isolation consist in chemical and radioisotope composition of radioactive waste products (RW). Low active and short-living medium active RW are meant for a near-surface or shallow burial underground disposal whereas HAW should be subject to a deep burial underground disposal [13, 14].

Table 1 demonstrates the compositions of liquid HAW from nuclear complexes of different countries. The analysis of these data has shown, that liquid HAW to a considerable extent differ in acidity, in the content of stable elements and radionuclides (for example, the content of transuranium elements (TUE) could vary within a very wide range from the values <0.1 up to 18 g/L, whereas for the fission products this value ranges from 1.0 to 87 g/L) [6, 15].

Radionuclides ^{90}Sr and ^{137}Cs almost completely decay already in 300 years (for 10 half-life periods). However in view of possible presence of a long-living isotope such as ^{135}Cs it is necessary to incorporate this fraction into mineral-like matrices resembling the natural granite by its properties in order to provide thus almost full ecological safety [16]. Taking into account the fact that the half-life period of one of the most long-living and toxic radionuclides such as ^{237}Np amounts to $2.14 \cdot 10^6$ years, the necessary period of HAW isolation within bowels should be longer than 20 million years. The potentialities of contemporary science forecast for such a long period of time is rather limited, therefore a real period of time providing guaranteed safety of burial ground HAW disposal according to the IAEA recommendations is considered to be as long as 10^4 years [17]. In this case it is meant that the engineering and geological barriers available are so reliable, that the probability of a considerably longer period of isolation is very high [18].

Half-life period value, biological hazard and chemical properties of HAW components to a considerable extent differ from each other; moreover, the comparison of HAW compositions and various types of rocks has shown that to match a geochemically compatible type of rock does not seem to be possible [19]. In this connection there are obvious advantages of developing the methods for the separation of liquid RW mixtures in order to obtain separate fractions. The concept of SF processing accepted in Russia provides for the extraction of transuranium element elements, as well as caesium and strontium from HAW.

From the standpoint of the environmental safety of a permanent burial within geological media the separation of radionuclides into the separate fractions similar with respect to the geochemical characteristics (alkali and alkaline-earth elements such as ^{137}Cs–^{90}Sr, rare-earth elements (REE) and actinoids), could allow one to choose for each fraction the rocks and the minerals capable to incorporate radionuclides into the structure [19].

Within the framework of the geoecological approach the following sequence of liquid HAW processing is considered to be optimum one:

– the storage in the liquid form for the reduction of the residual heat generation to a plausible level;

– the processing, including the fractionation of liquid HAW;

– solidification within mineral-like matrices those are optimum for separate fractions;

– final burial within stable geological formations; here both the matrix and host rocks should be in geochemical equilibrium.

The technology of RW burial conceptually differs from the technology of storage. The latter is based on the tight isolation of RW from biosphere whereas the technology of RW burial is based on the recognition of impossibility to guarantee the safety of engineering barriers during all the time of HAW storage (hundred thousand or even millions years) since the corrosion process can sooner or later disturb the tightness of packing to result in dispersing the radionuclides within the host medium [20]. In this connection the first and last barriers are of the most importance [11, 20].

The role of the last natural barrier is admittedly played by geological formations wherein a very slow dispersion of radionuclides up to a safe level is considered to occur. However, taking into account possible changes of geological conditions at the burial place after long time, the basic loading in preventing radionuclide from entering the environment falls at the first barrier whose reliability level is determined by isolating properties of a matrix. The chemical composition of rocks exerts a significant effect on the isolating properties of matrix materials, whereas the physical and chemical processes occurring within the system such as matrix with HAW–rock–underground waters can promote both an increase and decrease in the reliability of a burial. For minimizing the diffusion of radionuclides from a matrix into the environment the matrix should be to a maximum extent similar to host rocks of the burial place in the chemical and phase composition, *i.e.* it should be in the thermodynamic equilibrium with a host rock [11].

REQUIREMENTS IMPOSED UPON MATRIX MATERIALS

The matrix materials used for the binding of radioactive elements, firstly, should exhibit thermal stability at a high radionuclide content, mechanical durability, high heat conductivity, low thermal expansion coefficient and high resistance with respect to radiation damage; secondly, they should be stable with respect to the processes of physical and chemical weathering, pneumatolysis under the conditions of the burial place and, thirdly, the materials should be in the thermodynamic equilibrium with host rocks of the burial place for preventing the diffusion of radionuclides into the environment [2, 19]. The aforementioned requirements imposed upon solidified waste products are reflected in the State Standard GOST R 50926–96 (Highly active solidified waste products. General technical requirements). The matrix materials are also imposed with ecological and economic requirements as it follows: the materials should be non-polluting and inexpensive, whereas the technology for obtaining them should be simple enough.

For today there are no matrix materials satisfying all these requirements.

Nowadays the ceramics on the basis of the phases similar to natural minerals is, to all appearance, the most suitable material for permanent (more than 10^5 years) isolation of RW, therefore in order to immobilize the components of RW, crystalline and vitrocrystalline mineral-like ceramics materials are under an active development almost in all the countries possessing nuclear-power engineering [6, 9, 10, 21].

GEOLOGICAL ASPECTS OF SAFE RADIOACTIVE WASTE BURIAL

The principle of phase chemical conformity between the RW matrix and host rock of a burial place implies using as matrices the materials with similar chemical and thermodynamic behaviour with respect to host rocks of a burial place, *i.e.* the matrices should be similar to the minerals forming the rock under consideration [11]. Moreover, these minerals should contain stable isotopes those are the analogues of the elements meant for the burial (alkali, alkali-earth and rare-earth elements, as well as naturally occurring isotopes of uranium and thorium), and/or they should be the concentrators of the latter. In this case the reliability of permanent RW immobilization is provided not only by physical and chemical durability of crystalline mineral-like phases and engineering barriers, but also by the conservation of the geochemical equilibrium in the bulk of a mountain range. So, for example, the significant geochemical stability of a granite mountain range can be achieved due to the equilibrium established for several million years of its formation between granite rock and underground (interstitial) waters within the total bulk of the granite mountain range. In fact, the RW burial place in the form of boreholes or shafts filled with the blocks of crystalline ceramics represents an analogue of natural congregation of accessory minerals [22].

The advantage of crystalline rocks with respect to HAW burial consists in their high durability, resistance against moderately high temperatures, increased thermal conductivity. Mine tunnels within crystalline rocks can keep the stability during an almost unlimited time. Underground waters within crystalline rocks usually demonstrate a low salinity as well as an alkalescent reducing properties, which as a whole corresponds to the conditions required for the minimal solubility of radionuclides [18].

According to the principle accepted and implemented in Russia that consists in approaching the burial places for radioactive waste products to the places of the RW formation, the practical works on the assessment of geological conditions appropriateness for HAW and SF burial were carried out over the territories of the Krasnoyarsk Region (the Niznekansk mountain range, within the region of the Mining and Chemical Industrial Complex) and of the Chelyabinsk Region (RT-1 Factory at the IC "Mayak").

Basing on the complex geological and geophysical as well as hydro-geological carried out within the 1990ths by the organizations of the RF Ministry of Atomic Energy, the RF Ministry for Science and Technology, the Russian Academy of Sciences and the geologists of the Krasnoyarsk Region, the granitoids of the Niznekansk mountain range (NKMR) have been recognized to be the most promising geological formation for the completion of open and closed fuel cycles [23–25]. In 2001 at the Krasnoyarsk Territory a "Declaration on intentions for the construction of underground laboratory" has been prepared and approved at the Krasnoyarsk Territory.

The choice of the NKMR granitoids is caused by their high isolation properties, sufficient for the retention of radionuclides (in particular, caesium, plutonium, americium and neptunium) within a long period of time in the case of the destruction of multilayered engineering barriers [25, 26]. In order to determine the type of stable minerals specific for granitoids and capable to incorporate radionuclides into the crystal lattice, we are presenting below a detailed analysis of the mineral composition of granitoids including that for the Niznekansk granitoid mountain range, too.

MINERAL COMPOSITION OF GRANITOIDS

The term "granitoid" is used as a synonym of such rocks as granite, granodiorite and tonalite. Granitoids are characterized by the constancy of chemical composition, supersaturation with silica and increased potassium content in comparison with sodium. In the modern geological literature the term "granite" denotes magmatic holocrystalline rocks wherein the main rock-forming minerals are presented by quartz (SiO_2), K–Na and Ca–Na feldspars such as $KAlSi_3O_8$–$NaAlSi_3O_8$ (microcline/ orthoclase – albite) and $CaAl_2Si_2O_8$–$NaAlSi_3O_8$ (plagioclases). Also there are some Fe–Mg silicates, so-called dark-coloured minerals: most often it is black mica (biotite $K(Mg,Fe,Al)_3(Al,Si)_4O_{10}(F)_2$, in some varieties partly replaced by muscovite), less often it is hornblende, even less often there are pyroxenes. There are various quantitative mineralogical classifications of granites, different authors presenting different compositions for granite. This fact is caused by significant fluctuations of quantitative proportions between main rock-forming minerals within granite. Feldspars in granitoids add up to about 60 % of the bulk of rock, quartz content being as high as 30 %, and Fe–Mg silicates amounting to 10 % [27–29].

Tables 2 and 3 demonstrate the data on the content of the main rock-forming minerals in some magmatic rocks of the granite family as well as the chemical composition of these rocks.

A high content of SiO_2 (up to 77–78 mass %) is inherent in the total chemical composition of granitoids, *i. e.* granitoids belong to acid magmatic rocks. In addition, granites contain 13–18 mass % of Al_2O_3, 7–11 mass % with respect to the sum of $CaO + Na_2O + K_2O$ and up to several mass percent with respect to the sum of $Fe_2O_3 + FeO + MgO$.

The mineral composition of granite is rather manifold. Except for rock-forming minerals, granite contains accessory minerals (the minerals included in the composition of magmatic rocks in small amounts usually less than 1 %) such as apatite, zircon, sphen, magnetite, hematite, monazite, orthite. Sporadically there are prismatic crystals of hornblende observed. There can be garnet, pomegranate, tourmaline, topaz, fluorite, lithium micas, tinstone, wolframite, arsenopyrite, axinite, *etc*. among accessory minerals [31]. According to the mineralogical composition and structure one can consider syenites, especially nepheline syenites, to be closest to the rocks of granite family though the syenites belong to medium magmatic rocks (the content of silica amounting to 55–65 %) [30]. Nepheline syenites differ from granites by a lower content of silica, by full absence of quartz (instead of the latter the minerals contain nepheline at the rate of 15–30 %. From dark-coloured minerals they contain alkaline pyroxene (aegyrine, aegyrinaugite up to 10–20 %), alkaline amphiboles (hornblende, arfwedsonite, *etc*.), dark micas (biotite) and zeolites (sodalite quite often substituting for nepheline; less often one could observe nosean, hauyne, cancrinite, analcym). Constantly occurring accessory minerals include various

TABLE 2

Main rock-forming minerals of granitoids [27, 29]

Rock	Content of a mineral in rock, %			
	Potash feldspar (PF) (K,Na)$AlSi_3O_8$	Plagioclase $CaAl_2Si_2O_8$-$NaAlSi_3O_8$	Quartz SiO_2	Dark-coloured minerals (Fe,Mg silicates)
Leucogranite	45–50	20–25	25–30	2–5
Granite	30–40	25–30	≥30	5–10
Granodiorite	10–20	30–50	25–30	7–10
Tonalite	1–15	45–60	15–20	10–25
Diorite	0–5	60–80	0–5	25–40
Syenite	40–50	5–20	0–5	up to 40
Nepheline syenite	50–70	10–30	(quartz 0, nepheline15–30)	up to 15

TABLE 3

Chemical composition of magmatic rocks, mass % [29, 30]

Oxides	Leucogranite	Granite	Granodiorite	Tonalite	Diorite	Nepheline syenite
SiO_2	76.26	72.05	66.52	66.15	54.83	54.99
Al_2O_3	13.12	14.09	14.46	15.56	15.50	20.96
Fe_2O_3	0.75	2.01	4.77	4.78	7.27	4.3
MnO	0.02	0.07	0.08	0.08	0.12	0.15
MgO	0.14	0.53	2.20	1.94	8.08	0.77
CaO	0.49	1.33	3.75	4.65	5.77	2.31
Na_2O	3.76	3.62	3.31	3.90	3.34	8.23
K_2O	4.93	5.11	3.44	1.42	1.68	5.58
TiO_2	0.11	0.24	0.57	0.62	1.05	0.6
P_2O_5	0.01	0.07	0.15	–	0.44	–
Calcination loss	0.36	0.84	0.51	–	1.81	–

zirconium silicates and titanium silicates (zircon, sphen, apatite, less often fluorite) [31, 32].

Thus, granitoids mainly consist of rock-forming minerals such as feldspars (potash feldspars and plagioclases), quartz, micas, pyroxenes, amphiboles in various quantitative combinations. In addition, the composition of granitoids is characterized by a great variety of chemically stable and radiation resistant accessory minerals.

Petrographic and petrochemical studies on Niznekansk granitoid mountain range have allowed one to distinguish two petrographic associations of magmatic rocks within: one of them includes quartz diorites, granodiorites, low-alkali granites, granites and leucogranites, whereas another unites syenites, quartz syenites, subalkaline granites and leucogranites [33].

For the rocks of the first association, plagioclase prevails with respect to potash feldspar and quartz, there being amphibole and biotite among dark-coloured minerals. Accessory minerals are presented by apatite, sphen, orthite, zircon, titaniferous magnetite, magnetite and garnet. For the rocks of the second association potash feldspar with respect to plagioclase, amphibole is absent, and there being apatite, zircon, magnetite and rarely sphen among accessory minerals [33].

Taking into account this fact, within the framework of the geoecological approach the safe RW burial within a granitoid mountain range should be carried out using the matrices similar to stable minerals inherent in granitoids. Since the majority of naturally occurring minerals represent solid solutions due to their capability for isomorphic substitutions, it is worthwhile to use as binding matrices for RW elements such structural types of minerals whose solid solutions exhibit a high isomorphic capacity and are able to concentrate within the crystal lattice the fractions of radioactive waste products. Owing to the capability for isomorphic substitution of Na^+, K^+ or Ca^{2+} cations within feldspars and/or feldspathoids by various cations including the cations of Cs^+ and Cs^+, solid solutions based on the minerals such as feldspar and feldspathoids could be used for the immobilization of relatively short-living heat generating radionuclides such as strontium and caesium [11].

The testing for the resistance with respect to the leaching skeletonization (MCC-1, 90 °C) of some skeletal rock-forming minerals of granitoids has demonstrates a considerable stability of skeletal aluminium silicates: the leaching rate value for the majority of the components (Na^+, K^+ and Ca^{2+}) amounts to 10^{-7} g/(cm^2 · day) [34]. Upon exposure more than 50 days the leaching rate value for sodium from feldspars is quite comparable to the leaching rate value for caesium from synrock-C [35].

Accessory minerals such as monazite and zircon use to contain significant amounts of radioactive U and Th (up to 10 mass %) [6, 9]. They are very resistant against corrosion, leaching and radiation. The samples of such minerals are known whose age is estimated to be within the range of 2-4 million years. The initial dissolution rate value for zircon in a Soxhlet extractor varies within the range from $4.6 \cdot 10^{-9}$ (at 90 °C) to $4.1 \cdot 10^{-8}$ g/ (cm^2 · day) (at 250 °C) [9]. The corrosion rate for monazite in water is lower than $2 \cdot 10^{-7}$ g/ (cm^2 · day) at 90 °C under static conditions [36]; similar low corrosion rate values are inherent in synrock-C.

The analysis of minerals (Tables 4 and 5) wherein an isomorphic incorporation of radionuclides is possible, has demonstrated that for granitoids the alkaline and alkaline-earth radionuclides could be bound within the crystal lattice of the rock-forming minerals belonging to the aluminium silicate group (feldspars, feldspathoids, biotite, *etc.*), whereas the radionuclides from the group of REE and actinoids could be incorporated into plagioclases and micas, however they are mainly enter the accessory minerals, such as zircon, sphen, zirconolite, momazite, apatite, *etc.*

From the standpoint of the accessory minerals occurrence frequency for granitoids, of their isomorphic capacity and the ability to incorporate various radionuclides [12] the most

TABLE 4

Rock-forming and dark-coloured minerals of granitoids and the elements capable of isomorphic incorporation into minerals [11, 19]

Mineral	Mineral formula	Elements isomorphically binded in minerals
Orthoclases (K,Na feldspars)	$(K,Na)[AlSi_3O_8]$	Cs, Rb, Ge, Ba, Sr, Ag, Ln, Fe
Plagoclases (Ca,Na feldspars)	$(100-n)Na[AlSi_3O_8] \cdot nCa[Al_2Si_2O_8]$	Sr, Ge, Rb, Ag, Ba, Pb, Ln, Tl, Fe, Ga
Quartz	SiO_2	Fe, Al
Micas:		
Biotite	$K(Mg,Fe)_3[AlSi_3O_{10}][OH,F]_2$	Sr, Cs, Th, U, Ti, Na,
Muscovite	$KAl_2[AlSi_3O_{10}][OH]_2$	V, Li, Mn, Ba, Ln
Amphiboles:		
Hornblende	$Ca_2Na(Mg,Fe)_4(Al,Fe)[(Si,Al)_4O_{11}]_2[OH]_2$	Th, K, Ti, Ln
Arfwedsonite	$Na_3(Fe,Mg)_4(Fe,Al)[Si_4O_{11}]_2[OH,F]_2$	
Pollucite	$CsAlSi_2O_6$ (theoretically) $Cs_4NaAl_5Si_{11}O_{32} \cdot 1.3H_2O$	Cs, Rb, K, Tl

TABLE 5

Accesory minerals of granitoids and the elements capable for isomorphic incorporation into minerals [12, 31, 37]

Mineral	Mineral formula	Elements isomorphically incorporated into minerals	Possible radionuclides
	*Permanently occurring minerals (100–90 %)**		
Zircon	$ZrSiO_4$	Y, Ln, Th, U, Fe, Ca, Al, Hf, Nb, Ta, Sn, Be, Sr	Ln, An
Apatite	$(Ca,Ln)_5[PO_4]_3(F,OH)$	Th, Y, Ln, I(?), U, Na, Mg, Fe, Al	Sr, U, Ln
Magnetite	$Fe^{2+}Fe_2^{3+}O_4$	Mg, Al, Ti, Cr, Ni, Co	Tc^{4+}
Sphen	$(Ca,Ln)Ti[SiO_4]O$	Th, Mn, Fe, Mg, Al, Cr, Zr, Nb, Co?, Ni, Sr, Y, Zr, Ba, Ln, U	Sr, Ln, An
Garnet	$A_3^{2+}B_2^{3+}[SiO_4]_3$, A^{2+} = Mg, Fe, Mn, Ca; B^{3+} = Al, Fe, Cr	Na, K, P, V, Zr, Be	Ln, An, Sr, Ba, Zr
	Commonly occurring minerals (90–30 %)		
Orthite	$(Ca,Ce)_2(Al,Fe)_3[Si_2O_7][SiO_4]O[O,OH]$	Th, U, Na, Mg, Mn, Sc, Y, Be, La ...	Ln, An
Monazite	(Ce, La ...)PO_4	Th, Y, Ca, Mg, Fe, La, Pr, Nd, U, Sr	Ln, An Sr
Xenotime	YPO_4	Er, Ce ..., Th, U, Zr, Sn, Si, Ca	Ln, An
Thorite	$ThSiO_4$	U, Ln, Ca, Fe, P	Ln, An
	Rarely occurring minerals (30–0 %)		
Scheelite	$CaWO_4$	Mo, Cu, Ce, Pr, Nd ...	Sr, Tc^{6+}, Ln
Uraninite	UO_2	Ra, Ac, Po, Pb, Ce, Ln, Th, Zr	
Spodumene	$Li,Al[Si_2O_6]$	Na, Ca, Mg, Cr, Cs, Ln	
Perovskite	$CaTiO_3$	Fe, Al, Cr, Ce, Pr, Nd, Pm	Sr, Ru, Tc^{4+}, Ln, An
Chalcolamprite	$(Na,Ca...)_2(Nb,Ti...)_2O_6$ [F,OH]	Ta, Th, U, K, Mn, Fe, Ln, Sn, Zr, W, Sb, Mg, Pb, Hf, Si, Al, Sr, Be, Cu, Bi, Ge	Ln, An
Spinel	$MgAl_2O_4$	Fe, Mn, Zn, Ni, Co, Cr	Tc^{4+}
Kosnarite** [38]	$KZr_2(PO_4)_3$, structural analogue $NaZr_2(PO_4)_3$ (NZP)	Hf, Fe, Mn, Na, Rb, Zr, F	Cs, Sr, An, Ln, Ru, Tc^{4+}

Note. An – actinoids.

* Number of mineral revealing events in relation to the total number of the samples analyzed (%).

** Revealed within granitoid pegmatites.

suitable matrices for immobilizing lanthanoid and actinoid HAW fractions could be presented by silicate ceramics with the structure of such minerals as zircon $ZrSiO_4$ [9, 39], garnet $A_3^{2+}B_2^{3+}[SiO_4]_3$ [40], sphen $CaTi[SiO_4]O$ [41], as well as orthophoshate ceramics with the structural types of monazite (Ce,La...)PO_4 [9, 40–42], kosnarite $KZr_2(PO_4)_3$ (NZP) [43, 44], apatite $(Ca,Ln)_5[PO_4]_3(F,Cl,OH)$ [41, 45, 46], *etc.*

Ttitanate-containing mineral-like ceramics on the base of perovskite $CaTiO_3$ [12], chalcolamprite $(Na,Ca...)_2(Nb,Ti...)_2O_6$ [F,OH] [48], murataite $A_4B_3C_6O_{18}(OH,F)_4$ (A = Na, REE, Ca; B = Zn, Fe; C = Ti, Fe, Nb) [48, 49], *etc.* are considered to be promising thus being actively developed. However, despite of separate cases when the mentioned minerals are present in granitoids [37], they occur mainly in alkaline rocks such as alkaline basalts and nepheline syenites [31]. Thus, within the framework of the suggested geoecological and mineralogical approach to HAW burial within granitoid mountain ranges (for example, within the Niznekansk granitoid mountain range) and taking into account the world experience in testing different types of mineral-like matrices for immobilizing the alkaline and alkaline-earth elements of HAW the preference should be given to such minerals as skeletal aluminium silicates such as feldspars and feldspathoids, whereas for the immobilization of actinoids and lanthanoids one should prefer the minerals with the composition of $Me_m(PO_4)_n$ (monazite, zircon, kosnarite), as well as sphen and apatite.

MINERAL-LIKE MATRICES

The ceramic mineral-like materials with the structure of the aforementioned minerals actively developed within last 30–50 years, for example the matrices for caesium and strontium immobilizing, were obtained using various methods:

– by means of the sorption and phase transformation of zeolites (hot pressing, 800–900 °C, axial pressure amounting to 150–500 kg/cm^2, 1–2 h) [34];

– *via* the hydrothermal synthesis (650 °C, $P = 1.5$ kbar, 20 days) [50];

– through the metasomatic substitution within a “granite” matrix (the mixture either of grains albite and quartz grains or of microwedge and quartz + Na_3PO_4 grains, calcination at 1200 °C) [51];

– by means of granite and nepheline syenite mixture sintering (1020 °C, 24 h, the samples were preliminary were premolded at $P =$ 5 kbar) [52];

– applying the SHS technology(self-propagating high temperature synthesis, 1250 °C, the molar ratio $(TiO_2,Al_2O_3) : SiO_2 = 1 : 4$) [53].

The obtained ceramic matrices on the basis of skeletal aluminium silicates with the structure of fieldspars, nepheline and pollucite are resistant against leaching (the leaching rate value for caesium ranging within $4 \cdot 10^{-5}$–$6 \cdot 10^{-7}$ g/(cm^2 · day)), thus they and could be used as matrices for permanent immobilization of caesium and strontium.

The immobilization of actinoid HAW components was carried out within mineral-like matrices with the structure of apatite, kosnarite (NZP) and perovskite [12, 41, 42, 44, 54–56]. It has been demonstrated that the phosphate ceramics is resistant against the influence of high temperature and radiation, being insoluble in neutral and alkaline media and exhibits strong binding even with respect to such mobile radionuclides as Tc and Ra. The phosphate technology is comparable to cementation by its cost and capability for solidifying the mixed waste products of wide-graded composition, whereas the level of its realization corresponds to a pilot stage [41].

Also noteworthy are glass-ceramic forms of waste products are those are obtained using a controlled bulk crystallization of silicate glasses of corresponding structure with HAW and nucleating agent additives according to a sol-gel technology [41]. In this case radionuclides (up to 95 %) are immobilized within the crystalline component of a glass-ceramic material presented by various mineral-like phases. The glass-ceramic form of waste products wherein radioactive components represent a part of mineral phases, could be obtained also by through the capsulation of calcinated waste products or ready crystalline phases within an amorphous matrix, in this case within the vitreous phase. The presence of the vitreous phase causes glass ceramics to be more flexible with respect to variations in the structure of waste products and allows one to make lower the temperature and pressure of hot pressing. Furthermore, the vitreous phase is considered to be an additional barrier upon multibarrier burial of wastes.

According to the physical properties the glass-ceramic forms of HAW are considered to be at an intermediate position between borosilicate glass and synrock ceramics, being similar to the latter in radiation stability, and comparable to naturally occurring minerals and glasses in chemical stability. Owing to the combination of crystalline phases and a vitreous phase, there are low leaching rates provided for any radionuclide including the most mobile ones (such as ^{137}Cs).

Sphen-based titanium silicate glass ceramics, as well as glass ceramics on the basis of naturally occurring basalts and slag pyroceram containing aluminium silicate vitreous phase are considered among silicate compositions to be most thermally and chemically resistant as compared to other compositions [6].

Commonly used methods for obtaining ceramic and glass-ceramic matrices are complicated with respect to hardware implementation, they are multistage and rather power-consuming. The powder technology used in most cases for obtaining monomineral forms and polyphase ceramics, exhibits a number of disadvantages, first of all consisting in the occurrence of dust-generating and high-temperature (with the temperature higher than 1500 °C) stages. In this connection the problem of obtaining the matrices using cheap and available raw material through the application of simple energy-saving technologies with no disadvantages of the powder technology, remains still urgent.

One of the methods allowing one to transform radionuclides from a water-soluble state into a stable solid form consists in the use of porous inorganic materials. Microporous materials studied at different times (porous glass, silica gel, foamed corundum, diatomite, chamotte) for a number of reasons, one of those consisting in the use of high temperatures for the solid material saturation with LRW solutions, have found no wide application in radiochemistry.

For the successful application during the conditioning of liquid RW, porous materials should exhibit a high accessible porosity, regular porous structure, high moisture removal rate, resistance against concentrated acids, thermal stability, and prescribed chemical composition. Owing to these properties these materials can carry out several functions corresponding to certain stages of RW solidification process: 1) absorption of solutions within the bulk of a porous material due to capillary forces and a high wettability of internal surface; 2) water evaporation and its intense removal from a developed working surface at low temperatures; 3) repeated saturation by a solution at low salination of waste products in order to reach of a required level of filling; 4) decomposition of nitrates to result in oxide formation at the stage of calcination and reliable immobilization of radionuclides within the structure mineral-like phases at the final conditioning stage in the process solid-phase transformation.

Such multifunctional porous materials for LRW immobilization were obtained [57, 58] with the use of vitrocrystalline aluminium silicate components of volatile ashes from power stations which components represent hollow aluminium silicate microspheres (so called cenospheres).

MINERAL-LIKE MATRICES OBTAINING VIA MULTIFUNCTIONAL POROUS MATERIALS BASED ON CENOSPHERES

Cenospheres from volatile ashes by-produced at power stations structurally represent hollow spheres with a thin vitrocrystalline shell 5–10 μm thick on the basis of aluminium silicate glass (85–95 %) with the inclusions of minor amounts of quartz, mullite and ferriferous spinel phases [59]. According to the macro-componental composition the cenospheres are close to naturally occurring granitoids [60], which allows one to use them as precursors for the formation of skeletal aluminium silicate minerals such as feldspars and/or feldspathoids those could bind such radionuclides as caesium and strontium being geochemically compatible with host granitoid rocks under the conditions of permanent RW burial. The methods developed for the separation of cenosphere concentrates [61] allow one to isolate their narrow fractions within a certain range of silicon, aluminium and iron content the most plausible for obtaining the materials with prescribed properties.

Using the cenospheres with a stabilized composition the two varieties of porous materials are developed. They are porous aluminium silicate matrices of block type on the basis of consolidated cenospheres (Fig. 1, *a*, *b*) and microspheric zeolite sorbents (MZS) obtained by means of hydrothermal treatment of cenospheres (see Fig. 1, *c*).

The chemical composition of source cenospheres, porous matrices and MZS is presented in Table 6.

For solidifying the model solutions containing Cs or Sr those simulate liquid RW, porous matrices were used with the open porosity value of (63.6±1.3) % and with the specific surface area of (0.21±0.02) m^2/g [62]. It is shown that as the result of dosed introducing the solutions of caesium or strontium with the subsequent drying at a temperature of 130 °C and calcination of the saturated matrices at within the temperature range of 700–900 °C, *i. e.* at a temperature lower than the softening point for the matrix material, a solid-state crystallization of the matrix material occurs with the formation of the phases of the pollucite

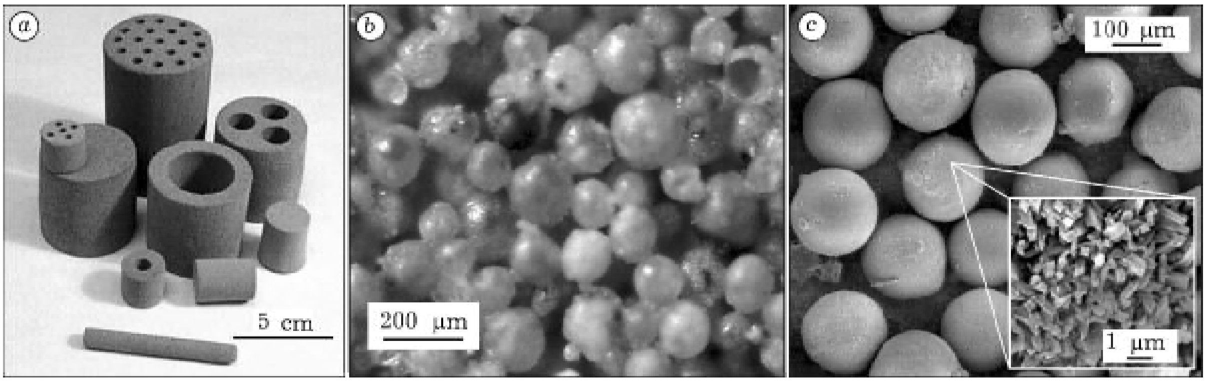

Fig. 1. Various modifications of porous aluminium silicate matrices *(a)*, the surface of porous matrices after saturation with nitrates and calcination (*b*) and microspherical zeolite sorbent (*c*).

TABLE 6

Chemical composition of initial cenospheres (IC), porous matrices (PM) and MZS formed under hydrothermal treatment (100 °C, 1.5 M NaOH, 72 h)

Sample	Chemical composition, mass %								Si/Al	Na/Al
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2		
IC	67.6	21.0	3.0	2.2	1.8	0.9	2.8	0.2	2.25	0.07
PM	66.3	19.2	3.4	2.6	1.9	2.2	2.1	0.6	3.04	0.16
Na-MZS	53.7	22.2	3.5	2.5	2.4	12.1	2.1	0.2	2.05	0.9

structural type (in the case of caesium introduction) and of the feldspar structural type (in the case of strontium introduction) with the conservation of the microspherical structure of porous matrices [62]. The in-matrix solidification of the solutions containing sodium and caesium with the prevailing amount of sodium compositionally corresponding to real RW proceeds with the crystallization of the nepheline type phases; in this case caesium is incorporated isomorphically into the lattice of these phases with the formation of Cs-containing nepheline [62]. The mass fractions of caesium and strontium introduced (recalculating into oxides) ranges within 3–28 and 6–17 mass %, respectively.

Figure 2 demonstrates X-ray diffraction profiles obtained for crystalline phases prevailing in porous matrices after the solid-phase transformation.

Basically, the further compacting of solidified products is possible with the use of different ways pressing techniques though the stability of the solidified products obtained to a complete extent meets the requirements of the Russian standards for solidified to highly active waste products purposed for permanent burial. The rate value for ^{137}Cs leaching from solidified at 700 °C (5 h) products (the content of Na_2O amounting to 4.4 and 8.3 mass %) within porous matrices detertmined according to the State Standard GOST 29114–91, is equal to $0.5 \cdot 10^6$ g/(cm$^2 \cdot$ day) (25 °C, 27 days)) [61], which meets the requirements of the State Standard GOST R 50926–96 for ^{137}Cs leaching from highly active solidified waste products (less than $1 \cdot 10^{-6}$ g/(cm$^2 \cdot$ day).

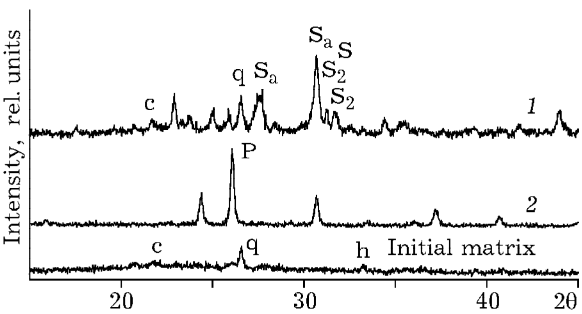

Fig. 2. X-ray diffraction profiles for the products from solid-phase transformations of porous aluminium silicate matrices with introduced caesium (*1*) and strontium oxides (*2*): *1* – 22 % Cs_2O, 700 °C, 5 h; *2* – 17 % SrO, 900 °C, 4 h; P – pollucite $CsAlSi_2O_6$; S_a – Sr-anorthite $SrAl_2Si_2O_8$; S – strontium metasilicates – α-$SrSiO_3$ and $SrSiO_3$; S_2 – strontium silicate Sr_2SiO_4; q – quartz α-SiO_2; c – cristobalite SiO_2; h – hematite Fe_2O_3.

The microspherical zeolite sorbents obtained by means of the hydrothermal treatment of cenospheres in alkaline medium [63] represent hollow spherical granules from 70 to 400 μm in size completely holding the spherical shape of initial cenospheres (see Fig. 1, *c*). The tests carried out at the Institute of Chemistry and Chemical Technology, SB RAS (Krasnoyarsk), and the Krasnoyarsk Mining and Chemical Industrial Complex, have demonstrated that the application (with the capacity up to 2 mg-eq/g of an adsorbent) is efficient for the extraction of Cs^+ and Sr^{2+} ions from subacid and neutral solutions [63].

The thermochemical transformation of MZS solid phase into crystalline aluminium silicates occurs at 500–1000 °C, the composition of the phases formed depending on the content of Cs^+ and Sr^{2+} and on the temperature of calcination. In the absence of caesium and strontium ions the initial Na-MZS under calcination (1000 °C, 4 h) yields nepheline (Fig. 3) [64]. In the case when the content of strontium is less than 50 mg/g of an adsorbent, one can observe the formation of nepheline-feldspar structures. In the case of increasing in the content of strontium up to 121 mg/g of an adsorbent the Sr-feldspar structure (see Fig. 3) is formed. Similar results were obtained for Cs-MZS, too. Heat treatment (1000 °C, 4 h) with the increase in the concentration of caesium adsorbed up to 174 mg/g of an adsorbent results in the crystallization from pollucite-nepheline structures to pure pollucite (see Fig. 3) [64].

The chemical stability of the products of solid-phase Cs-MZS crystallization also meets the requirements of the State Standard GOST R-50962–96 for ^{137}Cs leaching rate to be lower than 10^{-6} g/(cm$^2 \cdot$ day) [64].

Thus, it has been demonstrated that porous matrices and MZS obtained on the basis of cenospheres by-produced from coal combustion at thermal-power plants could be used for solidifying liquid Cs- and Sr-containing RW of various composition with the immobilization of caesium and strontium within the crystal lattice of rock-forming skeletal aluminium silicates such as fieldspars and feldspathoids, geochemically compatible with granitoids upon permanent burial.

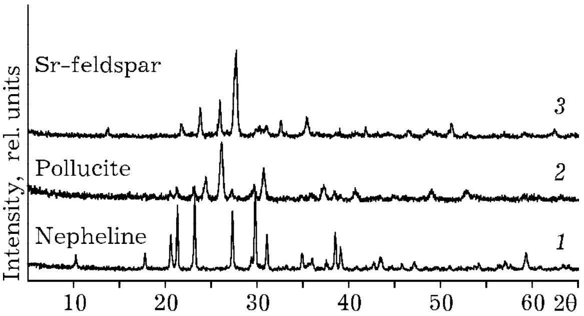

Fig. 3. X-ray diffraction profiles for the products from solid-phase crystallization of the initial zeolite adsorbent and MZS saturated with caesium (174 mg/g) and strontium (121 mg/g) cations: *1* – Na-MZS, 1000 °C, 4 h; *2* – Cs-MZS 1000 °C, 6 h; *3* – Sr-MZS 1000 °C, 5 h.

CONCLUSION

A geoecological approach is applied to the choice of mineral matrices for permanent burial of HAW within Nizhnekansk granitoid mountain range. It has allowed us to determine the stable minerals inherent in this granitoid mountain range those are capable to incorporate into the crystal lattice various fractions of radionuclides. They are rock-forming minerals such as feldspars and feldspathoids for such radionuclides as caesium and strontium as well as accessory minerals (zircon, sphen, kosnarite, *etc.*) for actinoid and lanthanoid fractions.

Variants for immobilizing liquid radioactive waste products within matrix materials of feldspar and feldspathoid structural types using a cheap and available aluminium silicate raw material are demonstrated. Multifunctional block porous matrices and powder microspherical zeolite sorbents have been obtained basing on cenospheres from ashes formed at power stations, which could allow one to transform water-soluble compounds of caesium and strontium (simply enough and under rather soft conditions with the temperature lower than 1000 °C) into mineral water-insoluble species of the predicted feldspar and feldspathoid structural types plausible with respect to permanent HAW burial within granitoids.

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