

Approaches to rehabilitation of radioactive contaminated territories

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Abstract

BACKGROUND: Accidents at nuclear fuel cycle plants may lead to contamination of areas of land and water. Cheap and available sorbents including natural aluminosilicates can be used for rehabilitation and decontamination of large volumes of radioactively contaminated water, including drinking water, prevention of migration of radionuclides into ground and surface waters through the soil and returning contaminated soil to farming.

RESULTS AND DISCUSSION: A comparative study of sorption properties of various natural and surface-modified aluminosilicates with respect to caesium is made. It is shown that sorption features of surface-modified aluminosilicates for Cs were improved by 100–1000 times compared with respective natural aluminosilicates. It is shown that surface modification of glauconite by a mixed nickel–potassium ferrocyanide phase allows it to considerably increase its specificity (caesium distribution coefficients $(2.9 \pm 0.8) \times 10^3 \text{ mL g}^{-1}$ for natural and $(4.5 \pm 0.5) \times 10^5 \text{ mL g}^{-1}$ for modified glauconite) as well as making it selective to caesium in the presence of other alkaline ions and also provides irreversible caesium sorption.

CONCLUSIONS: Due to improved features, modified aluminosilicates can be more successful than natural ones when used for rehabilitation of radioactive contaminated territories (including agriculture) and water areas, as well as for decontamination of liquid radioactive wastes and for creation of geochemical barriers in solid radioactive waste storage.

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Keywords: aluminosilicates; nickel–potassium ferrocyanide; rehabilitation of radioactive contaminated territories

INTRODUCTION

Accidents at nuclear fuel cycle plants lead to contamination of areas of land and water. In cases of serious accidents, International Nuclear and Radiological Event Scale levels 5–7, long-living radionuclides such as ^{137}Cs and ^{134}Cs make a major contribution to such contamination. Thus, large areas in Japan were radioactively contaminated as a result of the Fukushima incident. The density of pollution in the most contaminated territories is up to 25–30 kBq per kg of soil (represented by ^{137}Cs and ^{134}Cs). A map of area contamination by ^{137}Cs and ^{134}Cs in Japan after the Fukushima incident is presented in Fig. 1. The high population density in Japan, the absence of free land and the impossibility of massive resettlement opportunities determine the necessity for rehabilitation of the land and returning the soils to the farming industry.

The principle of differentiated use of land must be the basis of returning contaminated areas to the farming industry. Using various rehabilitation activities depends on the density of pollution, and the efficiency of such activities is to be determined experimentally.

In cases of very high density pollution (specific activity $> 2 \text{ Ci km}^{-2}$) ploughing of contaminated soil to horizons, unavailable for roots of plants, can be an effective method of rehabilitation. The main results of scientific research and development of agronomical methods that allow the decrease of contamination of farming production grown on radioactive contaminated soils within the territory of East-Urals Radioactive Track, have been described.¹

The process of decreasing radionuclide migration into plants was the displacement of the contaminated layer of soil to a subsurface layer at a depth of 80–100 cm without destroying the structure of soil and decreasing its fertility.

By liquidation of consequences of Mayak disaster in 1957 on the lands of East-Urals Radioactive Track with density of pollution $< 0.2 \text{ Ci } (^{90}\text{Sr})/\text{km}^2$ no restrictions of farming activities were imposed. It was advised to grow forage for beef cattle on land with a density of pollution $0.2\text{--}2 \text{ Ci km}^{-2}$ and to grow bread-corn as seeds on land with a density of pollution at $2\text{--}8 \text{ Ci km}^{-2}$.¹

Migration of radionuclides from soil to vegetation occurs through groundwater, therefore methods of retaining radionuclides in soils by the addition of sorption materials to soils can be effective for rehabilitation of areas with the aim of returning contaminated land to farming. Cheap and available sorption materials with good affinity to natural systems are needed for such rehabilitation. Natural aluminosilicates satisfy these requirements; interest and their intensive study are determined by their ion exchange properties and also by the availability of proven deposits in many countries. Natural aluminosilicates and some of their modified

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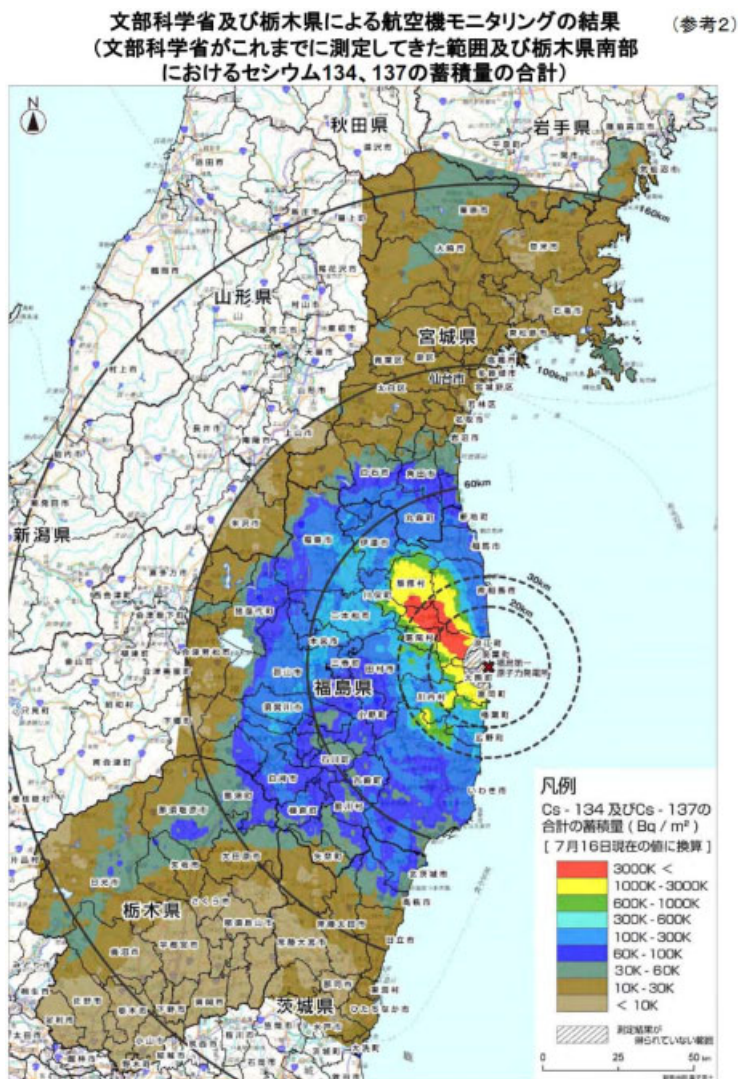


Figure 1. Map of areas contamination by ¹³⁷Cs and ¹³⁴Cs in Japan as a result of the Fukushima incident.

Table 1. Chemical composition of leachants

Ions	Concentration, mg L ⁻¹		
	Rain water	Tap water	Mineral water
pH	5.8 ± 0.2	8.2 ± 0.2	7.2 ± 0.2
K ⁺	3.7	3.6	400-900
Na ⁺	5.0	25.5	<50
Ca ²⁺	6.1	40.0	<25
Mg ²⁺	0.3	8.0	<75
Fe	-	1.8	-
Cl ⁻	4.6	16.5	300-600
HCO ₃ ⁻	-	-	<75
SO ₄ ²⁻	1.7	52.5	-
NO ₃ ⁻	1.6	-	-

products have been successfully used for decontamination of radioactive polluted natural waters and technological solutions, liquid radioactive wastes,²⁻¹⁴ and remediation of land under high anthropogenic impact.¹⁵⁻²⁰

If high caesium specific activity is present in natural water a high decontamination factor will be required; in the case of soil contamination high retention efficiency of radionuclides will be required to prevent their migration into vegetation and further movement through food chains. Therefore, the most important characteristics of sorption materials are specificity, measured as distribution coefficient *K_d*, selectivity and irreversibility of sorption. It is possible to increase sorption and mechanical features of natural aluminosilicates by their granulation and/or surface modification. Distribution coefficients of caesium for natural aluminosilicates and some of their modified products described in the above-mentioned works do not exceed 10³–10⁴ mL g⁻¹ and suggested methods of rehabilitation do not take the behaviour of these sorbents in the environment and the reversibility of radionuclide sorption into account.

It is possible to improve sorption and mechanical features of natural aluminosilicates and make caesium sorption irreversible via surface modification of these aluminosilicates with ferrocyanides.

A comparative study of caesium sorption by clinoptilolites from Shivrtoovsky (Chita region, Russia) and Dzegvi (Georgia) deposits, quartz-glaucanite concentrate from Karinskoye deposit (Russia), zeolite from Sibai deposit (Bashkortostan, Russia), vermiculite

Table 2. Chemical composition (%wt) of aluminosilicates studied. Relative errors < 10%

Aluminosilicate	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	MnO	CaO	TiO ₂	Na ₂ O	K ₂ O
Clinoptilolite; Shivyrtsoosky deposit (Chita region, Russia)	74.5	14.89	1.49	0.34	0.62	0.40	1.08	0.19	3.02	3.34
Clinoptilolite; Dzegvi deposit (Georgia)	75.3	15.07	–	–	0.3	–	0.8	–	6.4	2.1
Quartz-glaucanite concentrate; Karinskoye deposit (Russia)	71.0	6.4	18.6	–	2.2	0.015	0.8	0.14	~0.2	–
Zeolite; Sibai deposit (Bashkortostan, Russia)	64.8	11.0	–	–	–	–	10.0	–	5.6	8.5
Vermiculite; Buldymoskoe deposit (Russia)	46.35	15.9	6.57	2.93	24.29	–	1.45	0.98	–	1.61
Manganese Greensand sorbent (glaucanite sand, USA)	76.0	5.5	20.0	–	1.8	0.5	0.7	0.1	~2.0	–

Table 3. Distribution coefficients of caesium for natural and modified aluminosilicates

Sorbent	Distribution coefficient of Cs (K _d), mL g ⁻¹ ; τ = 1 week (unless otherwise indicated)
1. Natural aluminosilicates	
Clinoptilolite; Shivyrtsoosky deposit (Chita region, Russia)	$(6.4 \pm 0.6) \times 10^3$ (1.4 ± 0.1) $\times 10^4$ (3 weeks)
Clinoptilolite; Dzegvi deposit (Georgia)	$(7.9 \pm 1.6) \times 10^3$ (1.3 ± 0.1) $\times 10^4$ (3 weeks)
Quartz-glaucanite concentrate; Karinskoye deposit (Russia)	$(2.9 \pm 0.8) \times 10^3$
Zeolite; Sibai deposit (Bashkortostan, Russia)	$(3.1 \pm 0.6) \times 10^2$
Vermiculite; Buldymoskoe deposit (Russia)	$(1.2 \pm 0.1) \times 10^3$
Manganese Greensand sorbent (glaucanite sand, USA)	$(4.0 \pm 0.8) \times 10^3$
2. Surface-modified aluminosilicates	
NPF-clinoptilolite	$(5.0 \pm 4.0) \times 10^6$
NPF-glaucanite	$(4.5 \pm 0.5) \times 10^5$

(Russia) and manganese greensand (glaucanite sand, USA) and also surface-modified sorbents based on glaucanite and clinoptilolite is made in this work. The assessment of possibility of use of natural and modified aluminosilicates for rehabilitation of radioactive contaminated territories is made.

EXPERIMENTAL

Aluminosilicates from various deposits with grain sizes 0.2–0.6 mm were used for the study. Mixed nickel–potassium ferrocyanides based on glaucanite and clinoptilolite were obtained using surface chemical modification. This method includes the steps of chemical activation of natural aluminosilicate, sorption saturation by nickel ions and further treatment by K₄Fe(CN)₆ solution. Theory of this method has been described.^{21,22}

To study the caesium interphase distribution for natural and modified aluminosilicates, the following parameters were used: tap water spiked by ¹³⁷Cs; volume (V) = 50 mL, sorbent weight (m) = 100 mg, pH = 7.8 ± 0.2. Initial range of caesium concentrations in solution (10⁻⁷–1000 mg L⁻¹) were obtained using standard solutions of CsCl. Samples were measured via beta-radiometry using low background alpha-beta-radiometer “UMF-2000” with a semiconductor detector.

Selectivity of natural and surface-modified glaucanite with respect to caesium in presence of analog ions K⁺ and Na⁺ was studied at an initial caesium concentration of 0.01 mg L⁻¹. Experiments were performed under static conditions in water solutions spiked by ¹³⁷Cs; with alkali metal ion solutions obtained

using standard solutions of NaCl, KCl, CsCl. Duration of phase contact was 1 week.

The chemical stability of the saturated samples was determined using the long-term leaching technique. The sample of sorbent saturated by caesium labelled with radioactive ¹³⁷Cs was placed in a polyethylene container and filled with leachant. Sampling was made after 1, 3, 7, 10, 14, 21 and 28 days from the beginning of experience. The leachant was transferred to a container for subsequent analysis and the sorbent was washed out using the same leachant, filled with a fresh portion of leachant, closed and left for the next time. The content of caesium in the test was determined via γ-spectrometry. The leachants used were: rain water representing a natural water with very low salt content; tap water as an analogue of natural water with low salt content and relatively high iron content, and a natural mineral water with sodium hydrocarbonate-chloride mineralization, salinity 1.5 g L⁻¹. Chemical composition of these leachants is presented in Table 1.

RESULTS

Chemical composition of natural aluminosilicates, calculated for dry matter, is presented in Table 2.

Exchange capacity of aluminosilicates depends on Al/Si ratio and concentration of Na⁺, K⁺, Ca²⁺, Mg²⁺ ions located in interstices of lattice in a hydrate environment. Greater exchange of Al³⁺ ions in a mineral by iron or magnesium ions leads to additional compensation of electric charge by cations and therefore to increasing exchange capacity.²³ Ion exchange features

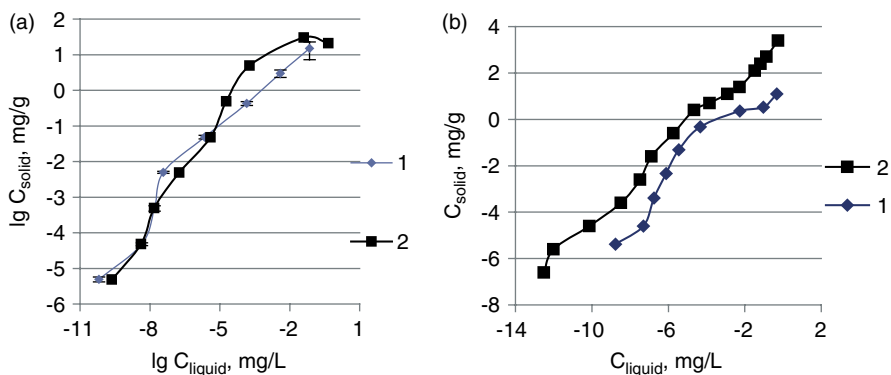


Figure 2. Isotherms of sorption of caesium from tap water: (a) natural aluminosilicates (1 = glaucanite, Russia; 2 = clinoptilolite, Russia), (b) surface-modified aluminosilicates (1 = based on glaucanite (NPF-glaucanite); 2 = based on clinoptilolite (NPF-clinoptilolite)).

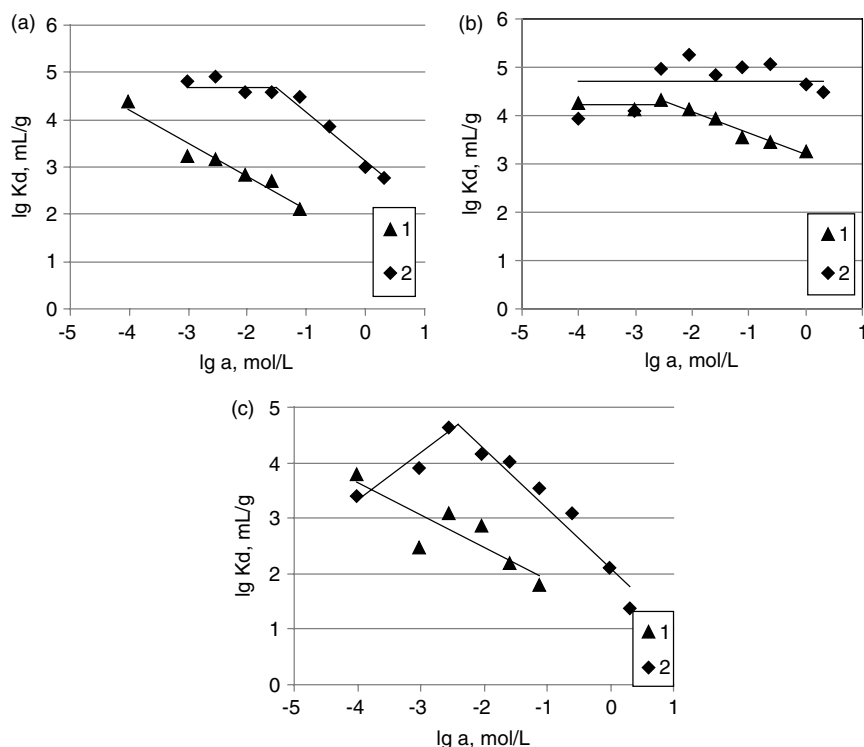


Figure 3. Dependences of caesium distribution coefficients K_d on active concentration a of K^+ (a), Na^+ (b) and NH_4^+ (c) in solution for natural (1) and surface-modified (2) glaucanite.

of aluminosilicates depend on degree of ions replacement, Al/Si ratio as well as on peculiarities of interstices and channels and ratios between their sizes and diameters of exchanging ions. Stability of aluminosilicates increases with decrease of Al/Si ratio.²⁴

Analysis of chemical composition has shown that clinoptilolite and vermiculite possess the most sorption exchange capacity; clinoptilolite possesses higher mechanical strength and chemical stability.

Distribution coefficients of caesium, determined under static conditions and for various durations of saturation, for natural and modified aluminosilicates are presented in Table 3. Data from Table 3 show that various aluminosilicates have various specificities with respect to caesium. The highest distribution coefficients are found for clinoptilolites. It is also obvious, that sorption by these materials can be increased up to 100–1000 times via surface modification by ferrocyanides. For example, the caesium distribution coefficient for

mixed nickel–potassium ferrocyanide on clinoptilolite can reach $(5.0 \pm 4.0) \times 10^6 \text{ mL g}^{-1}$, meanwhile for natural clinoptilolite this coefficient is only $(6.4 \pm 0.6) \times 10^3 \text{ mL g}^{-1}$.

Typical examples of caesium sorption isotherms by natural (a) and surface-modified (b) clinoptilolite and glaucanite from tap water (duration of saturation $\tau = 1$ week) are presented in Fig. 2. Isotherms of caesium sorption were made in 'lg C_{solid} –lg C_{liquid} ' axes (where C_{solid} is concentration of caesium in sorbent, mg g^{-1} and C_{liquid} is concentration of caesium in solution, mg L^{-1}) and described by the Langmuir isotherm. Direct proportion between concentration of caesium in sorbent and solution is observed at a certain concentration range for samples of natural glaucanite and clinoptilolite as well as for NPF-glaucanite.

Zones of linearity of isotherms coincide for natural and modified glaucanite. The isotherm of caesium sorption by NPF-clinoptilolite is a three-stage curve. Slopes of each straight-line portion of this

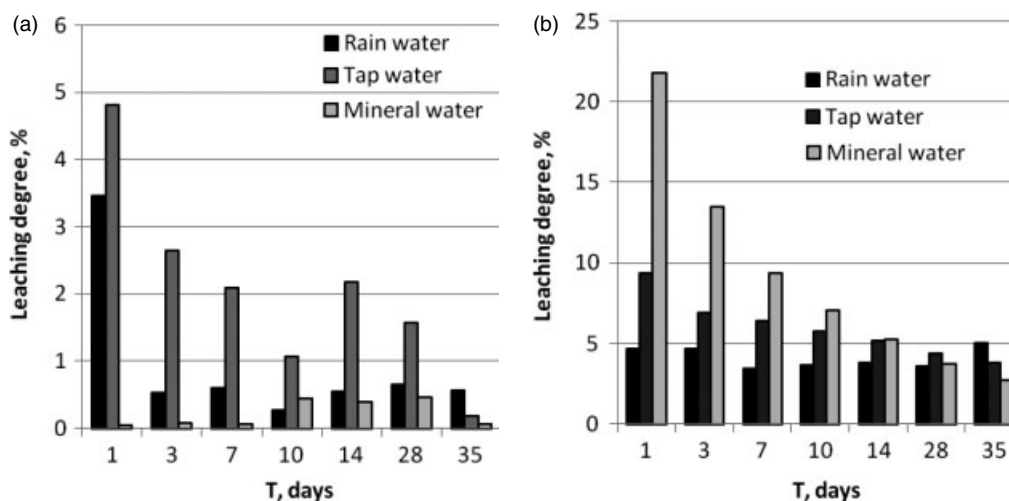


Figure 4. Time dependency of leaching of ¹³⁷Cs by various leachants from surface-modified glauconite (a) and natural glauconite (b).

curve are equal to 1 within limits of error, i.e. evidence of fulfillment of Henry's law. The form of the isotherm shows that this sorbent has three types of sorption sites and filling of each sorption site can be described by the Langmuir isotherm. The first type of sorption site with $\lg K_d = (7.4 \pm 1.3)$ is realized at caesium concentrations $1 \times 10^{-7} - 10^{-5} \text{ mg L}^{-1}$, the second with $\lg K_d = (5.1 \pm 0.3)$ is realized at $1 \times 10^{-4} - 1 \text{ mg L}^{-1}$, and the third with $\lg K_d = (3.5 \pm 0.2)$ at $10 - 1000 \text{ mg L}^{-1}$. Static exchange capacity of NPF-clinoptilolite is 500 mg of Cs per g of sorbent. A few points in the first linear portion of the isotherm give a large error in the calculated K_d , however, the K_d is not less than 10^6 mL g^{-1} . The caesium concentration range at which the most specific sorption site is realized corresponds to the normal concentration range of caesium in natural waters, usually within $10^{-9} - 10^{-7} \text{ g L}^{-1}$ ²⁵ which is important for application of the sorbent.

Dependences of caesium distribution coefficients K_d on active concentration a of K^+ (a), Na^+ (b) and NH_4^+ (c) in solution for natural and surface-modified glauconite are presented in Fig. 3.

Experimental data show that natural glauconite does not possess caesium selectivity so interference of sodium becomes apparent at concentrations of 0.01 mol L^{-1} and higher, whereas potassium shows some interference over all the concentration range. The interference of sodium with sorption of caesium by surface-modified glauconite is almost absent, allowing more efficient use of this material for separation of ¹³⁷Cs from natural waters, because sodium is one of main cations, together with calcium and magnesium in all natural waters. In contrast to sodium, potassium shows interference with sorption of caesium by surface-modified glauconite at concentrations of $0.03 - 0.1 \text{ mol L}^{-1}$ and higher, though distribution coefficients of caesium on modified glauconite remain considerably higher than those on natural glauconite. However, potassium is usually present in natural waters at lower concentrations than sodium with the average potassium concentration up to 0.01 mol L^{-1} in sea-water and rather lower (100–1000 times) in fresh and ground waters,²⁶ therefore in real situations potassium will show interference with caesium sorption only when natural aluminosilicates are used.

Ammonium ions show the strongest interference with sorption of caesium by both natural and surface-modified glauconite. NH_4^+ ions decrease sorption of caesium by natural glauconite over all studied concentration ranges, and their interference with sorption

by surface-modified glauconite is absent at concentrations less than 0.003 mol L^{-1} . Usually, ammonium ions are present in soils at low concentrations, but ammonia salts are often used as fertilizers. Therefore it is recommended to use nitrate fertilizers instead of ammonia salts, if surface-modified or especially natural aluminosilicates are used for rehabilitation of contaminated agricultural lands.

The degree of leaching of the radionuclide from samples saturated by this radionuclide allows an indirect conclusion about the reversibility of caesium sorption by natural and surface-modified glauconite to be drawn. The results of leaching of ¹³⁷Cs by various leachants from saturated samples are presented in Fig. 4.

The results obtained show, that high caesium leaching rates and degrees are typical for natural glauconite irrespective of leachant salinity. Total degree of leaching after 35 days was: mineral water = 63.4%, tap water = 41.6% and rain water = 28.8%. Thus, it could be expected that there will be no reliable retention of caesium by the solid phase after addition of the natural aluminosilicates into soil. In contrast to natural glauconite, the modified glauconite shows rather better results with the total degrees of leaching under the same conditions: mineral water = 1.5%, tap water = 14.6% and rain water = 6.6%. Therefore ferrocyanide surface modified glauconite can be used for rehabilitation of land contaminated by radiocaesium.

DISCUSSION AND CONCLUSIONS

Migration of radionuclides from soil to vegetation occurs through ground water therefore addition of sorbents to soils that are able to reliably sorb caesium and decrease its content in ground water is the only technically feasible way to prevent caesium migration into vegetation. Experiments have shown that modified aluminosilicates will be rather more efficient than natural materials for rehabilitation of radioactive contaminated land and returning the soils to farming. Thus, surface modification of glauconite by a mixed nickel–potassium ferrocyanide phase allows it to considerably increase its specificity as well as making it selective to caesium in the presence of other alkaline ions and also provide irreversible caesium sorption. The only drawback to using modified glauconite for rehabilitating contaminated agricultural land will be some limitation on the amount of inorganic potassium and ammonium fertilizers being used.

Currently the modified glauconite produced by the authors is being tested at radioactively contaminated areas near Fukushima in Japan. The first results are expected in the autumn of 2013.

As well as the above, modified aluminosilicates can be successfully used for decontamination of large volumes of radioactively contaminated natural water including drinking water, low- and middle-level liquid radioactive wastes as well as the creation of geochemical barriers in solid radioactive waste storage and limiting the migration of radioactively contaminated waters into the lithosphere.

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