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# Nuclear power industry and the environment

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**The new trends in the development of nuclear power industry are summarized with the special focus on their effects on the environment.**

To a considerable extent, the discovery of radioactivity by Henri Becquerel, Pierre and Maria Curie at the beginning of the XX century determined the further development path not only of natural science but of the human civilization in general. A great Russian scientist and thinker V. I. Vernadsky was among the first to understand and appreciate the importance of this discovery. He said in his well-known speech at a meeting of the Academy of Sciences in 1910: '...radioactivity phenomena are now opening atomic energy sources that are millions of times more powerful than any power sources that human imagination could have pictured'.[1] Nowadays, we do know how true these Vernadsky's words were. Radioactive nuclides and compounds, instruments and mechanisms based on them are widely used in scientific studies, have broad industrial applications, and are used in medicine and biology for diagnostics and treatment of various diseases. Nuclear industry that delivers both civil and military products has been created and successfully operates in advanced countries all over the world.

The history of radiochemistry development can be tentatively divided into three periods.[2] The first period (1896–1949) covers the origination and development of radiochemistry as a separate scientific direction. It is closely related to the discovery of radiochemistry, study of fundamental laws of this phenomenon, and determination of the main regularities in the behaviour of radioactive compounds.

The second period of radiochemical studies (1940–1970) involved the practical mastering of nuclear energy, studies on the chemical properties of artificial chemical elements (plutonium, neptunium, americium and others), creation of technologies for treatment of spent nuclear fuel (SNF), attempts to solve radioactive wastes (RW) management problems, *etc*. It is in this period that a huge amount of radionuclides, including particularly hazardous long-lived isotopes of transuranium elements, was discarded to the environment.

Finally, in the 1970s, the third stage of radiochemistry development began due to intense growth of nuclear power industry, when, as V. I. Vernadsky predicted, the humankind entered the phase of global impact on the environment. In this period, ecological problems related to environment protection from radioactive pollution and storage of RW gained utmost importance.

### Contemporary nuclear power industry and the nuclear fuel cycle

Commercial exploitation of nuclear energy began with the start-up of the first 5-MW (in electric power units) nuclear power plant in USSR in 1954. In 2013, according to data from International Atomic Energy Agency (IAEA), 434 nuclear power plants were operating in 30 countries worldwide. Totally they were producing 371.7 GW of electric power.[3] Recently Republic of Belarus became the second new country that started building its first nuclear power plant. The number of reactors being built in 2013 (72) was record-high since 1989. Of these, 48 reactors are located in Asia, and 42 of the last 52 new reactors that have been connected to power networks since 2000 are also located there.

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† The Editorial Board and Staff of Mendeleev Communications take an opportunity to congratulate Academician B. F. Myasoedov on the occasion of his 85th birthday and wish him all the very best.

According to the forecasts of the same Agency, the growth in nuclear power industry sector by 2030 will be from 17% (pessimistic scenario) to 94% (optimistic scenario). In Russia, 33 nuclear power units in ten nuclear power plants were in operation by the end of 2014. Their total rated output power was 23.6 GW, which corresponds to *ca*. 13% of the total electric power produced in the country.

**RW management**. The problem of SNF and RW management is among the factors that adversely affect the further development of nuclear power industry. Currently, concepts of open and closed nuclear fuel cycle (NFC) exist. According to the former, which is accepted in USA, Sweden, Finland and Switzerland, SNF is not reprocessed but is stored in special repositories with possible reprocessing or eventual geological burial in the future. More than 200 thousand tons of SNF have already been accumulated worldwide. It will be stored till a final decision on its fate is taken. At the same time, the SNF amount annually increases by about 8 thousand tons.[4] In the majority of other countries with developed nuclear power industry, such as France, Great Britain, Japan and Russia (pilot plants exist in China and India), SNF is subjected to reprocessing with extraction of uranium and plutonium by the PUREX (Plutonium-Uranium Extraction) process followed by solidification of the liquid RW.[5] The bases of this technology using 30% TBP in hydrocarbon diluents were developed in USA about 60 years ago for reprocessing of irradiated natural uranium for military purposes.

Calculated data on the decrease in the potential long-term effect on the environment in case of SNF disposal, on the one hand, and RW formed in a closed NFC with separation of fissile actinides ($^{239}$Pu and $^{235}$U) for their re-use in nuclear industry and minor actinides ($^{237}$Np, $^{241}$Am, $^{244}$Cm) for transmutation in fast neutron reactors, on the other hand, are shown in Figure 1.[6]

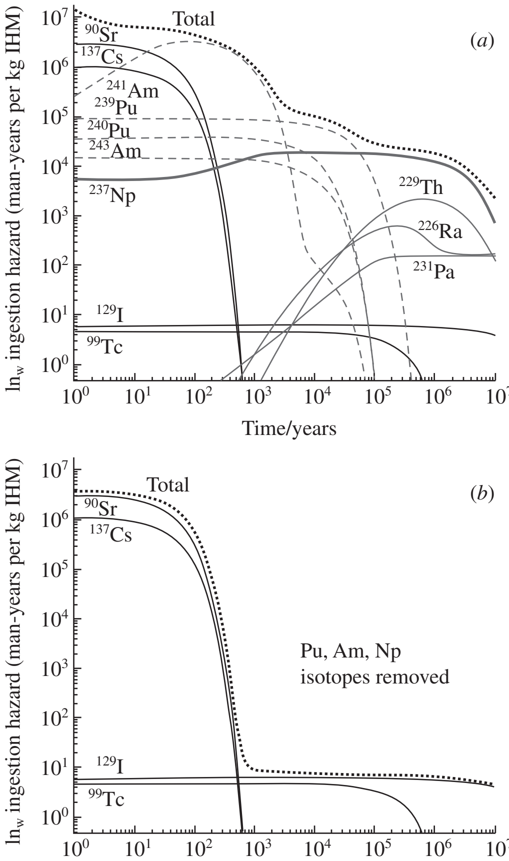


**Figure 1** Radiotoxicity variation with time: (*a*) starting SNF, (*b*) RW formed after separation of actinides.

**Table 1** Properties of the longest-lived toxic isotopes of actinide elements contained in SNF.

| Radionuclide | $T_{1/2}$/years | Type, energy and probability of the most intense radiation/keV |
|---|---|---|
| $^{233}$U | 1.59×10$^5$ | α: 4783 (0.132); 4824 (0.844) |
| $^{235}$U | 7.04×10$^8$ | γ: 143.7 (0.11); 185.7 (0.572)<br>α: 4366 (0.17); 4397 (0.55) |
| $^{238}$U | 4.47×10$^9$ | α: 4151 (0.21); 4198 (0.79) |
| $^{237}$Np | 2.14×10$^6$ | α: 4771 (0.25); 4788 (0.47) |
| $^{238}$Pu | 87.7 | α: 5456 (0.29); 5499 (0.71) |
| $^{239}$Pu | 2.42×10$^4$ | α: 5105 (0.115); 5144 (0.151); 5157 (0.733) |
| $^{240}$Pu | 6.56×10$^3$ | α: 5124 (0.27); 5168 (0.73) |
| $^{241}$Pu | 14.3 | β: 20.8 (max.) (1) |
| $^{241}$Am | 432.2 | α: 5443 (13%); 5486 (0.85)<br>γ: 59.5 (0.359) |
| $^{243}$Am | 7.37×10$^3$ | α: 5233 (0.11); 5275 (0.874)<br>γ: 74.66 (0.682) |
| $^{242}$Cm | 162.9 days | α: 6069 (0.25); 6113 (0.74) |
| $^{244}$Cm | 18.1 | α: 5763 (0.24); 5805 (0.76) |

As follows from the data in Figure 1 showing the variation in RW radiotoxicity with time, the radiotoxicity decreases by many orders after isolation of long-lived actinides from SNF in comparison with that of the original SNF.

High level radioactive wastes (HLRW) are generally solutions and sludges containing fission products (FP), such as isotopes of Cs, Sr, Zr, Tc, Mo, Ru, I, REE, as well as radionuclides formed upon decay of these FP, activated corrosion products (Cr, Mn, Fe, Co, Ni and Zr radionuclides), residual amounts of U, Pu and minor actinides (Np, Am, Cm). Table 1 presents the properties of the most hazardous actinide isotopes in RW after SNF reprocessing.

As one can see from these data, most isotopes of actinide elements are alpha emitters with long half-life periods and they present the highest ecological hazard. In fact, the high radiotoxicity of plutonium dictates its extremely low acceptable levels in natural waters: the intervention level for $^{239}$Pu is 0.55 Bq kg$^{-1}$.

Due to the high radiation hazard and chemical toxicity of HLRW, their subsequent storage requires conversion to a safer form. HLRW vitrification is the most acceptable technology, the only one developed to the stage of industrial application by now. It involves processes of drying, calcination, fusion with glass-forming additives in specialized ovens (melters) and filling of cans for long-term storage. The vitrification technology is used for solidification of HLRW in France, Russia, Great Britain, USA, *etc*. Borosilicate-based glass is used in the majority of countries, while alumophosphate-based glass is used in Russia.[7]

The choice of the matrix material composition for HLRW immobilization primarily depends on the chemical composition of the HLRW, on the type of the melter and other equipment used, on geological conditions of subsequent storage, *etc*. Two types of HLRW are currently subjected to vitrification: those formed upon SNF reprocessing and accumulated ‘historical’ HLRW from the past defense activities (production of weapon-grade plutonium). Borosilicate glasses have a set of physicochemical properties that allow them to be used for immobilization of the majority of HLRW components. They have high chemical and radiation stability, good mechanical strength, thermal conductivity, viscosity and electrophysical characteristics. On the other hand, they feature low dissolving ability for actinides, REEs and some transition elements. Alumophosphate glasses obtained at lower temperatures (800–1000 °C) can dissolve larger amounts of these HLRW components than borosilicate glasses that are obtained at 1050–1200 °C. However, alumophosphate glasses are characterized by stronger viscosity variation with temperature and exhibit smaller crystallization resistance. Furthermore, they have smaller regions of glass compositions with high chemical resistance. The choice of alumophosphate glass in Russia was largely determined by logistical reasons. It is well known that silicon does not form water-soluble compounds, except for sodium silicates (liquid glass), which cannot be used as a glass-forming additive due to the presence of sodium salts in liquid HLRW. Special tools are required for dosage of insoluble silicon compounds, whereas in the case of alumophosphate glass, liquid HLRW and glass-forming phosphorus compounds can be directly loaded onto the melt surface in the melter, which considerably simplifies the technology.

The leaching rates of Cs, Sr and actinides, both from borosilicate and alumophosphate glasses, are characterized by values of $10^{-5}$–$10^{-7}$, $10^{-6}$–$10^{-8}$, $10^{-7}$ g cm$^{-2}$ day$^{-1}$, respectively, or less. The β/γ irradiation by doses up to $10^7$–$10^9$ Gy does not increase the leaching rates by more than an order. Incorporation of short-lived actinide isotopes does not cause degradation of the glass materials or increase the leaching rates of HLRW either.[8–10]

Vitrification of HLRW is performed in industrial units with melting pots, with wall heating from an external inductor operating at a frequency of about 20 kHz (France, Great Britain) and in so-called Joule heated ceramic melters (direct heating electric tank furnaces) where electric current is passed through the glass melt (USA, Russia, Germany, Japan, India). To intensify the process and to reduce equipment size, variants of induction melting in cold pot (IMCP) at frequencies of 0.1–2 MHz, microwave (1–3 GHz) and plasma melting are considered.[7]

In the 1970s, an alternative concept was suggested in Australia for HLRW solidification in titanate ceramics (Synroc) based on zirconolite $CaZrTi_2O_7$, perovskite $CaTiO_3$, hollandite $BaAl_2Ti_6O_{16}$, rutile $TiO_2$ phases and metal alloys.[11] This mineral-like association makes it possible to accumulate all HLRW components by means of isomorphous substitutions. It was planned to obtain it by cold compaction and baking or by hot compaction at a pressure of 14–21 MPa at 1150–1200 °C. However, the process has not been implemented on industrial scale, except for a small plant in Australia for processing of wastes from $^{99}$Mo production.[12]

In recent years, intense studies on the use of crystalline double magnesium–potassium orthophosphate (MPP) as synthetic matrices for long-term and ecologically safe storage (or disposal) of liquid RWs, including actinide-containing wastes, were carried out in USA[13] and in Russia.[14–16] It is known that natural phosphate minerals (monazite, apatite) containing natural uranium and thorium in concentrations up to tens of mass percent possess high physicochemical stability in geological environments. This indicates that the use of synthetic analogues of minerals as matrices for RW immobilization is a promising approach. The non-thermal process for the preparation of MPP matrices (room temperature, ambient pressure) is similar to cement grouting and is characterized by small energy consumption, simple implementation and mobility of the hardening process. Furthermore, the simplicity of instrumentation minimizes 'secondary' RWs. The use of MPP provides some noticeable advantages: the possibility to solidify wastes in a broad pH range, high filling ratio of the matrices with RW components, high chemical and radiation resistance, stability to low temperatures.

Argonne National Laboratory (ANL, USA) has developed phosphate materials based on MPP for radiation protection shielding, binding materials for cementing of oil wells, for building industry and dentistry, and studied phosphate matrices for incorporation of low-radioactive waste simulators, plutonium- and technetium-containing wastes.[13,17] Researchers from Radium Institute (St. Petersburg, Russia) together with experts from INEEL (USA) studied the prospects of incorporating simulators of low-activity ash residues from combustible RW into iron-phosphate 'low-temperature ceramics'.[18] A new efficient technology for immobilization of RW with various compositions and sources, including those containing long-lived actinide isotopes, into MPP matrices have been developed at GEOKhI RAS (V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences) in collaboration with PA 'Mayak' (Central Plant Laboratory of Production Association 'Mayak'), with participation of ANL and CH2MHill company (USA).[16,19] High chemical stability of MPP matrices towards leaching of radionuclides and other components under the action of various leachants and temperatures was established. Mechanical and radiation stability of the matrices as well as the chemical yield of radiolytic hydrogen were determined. Data on the phase constitution and the character of distribution of the radionuclides in the matrix volume were obtained.[14–16]

Recently, the possibility of deeper HLRW fractionation has been actively discussed. Since HLRW contain both long-lived components (actinides) and comparatively short-lived fission and corrosion products, it seems expedient to separate HLRW components into fractions, in particular, to separate long-lived transuranium elements (about 5–10 kg per 1 ton of SNF) from fission and corrosion products. It is suggested to incorporate the actinide fraction into ceramic matrices that will remain stable for up to one million years, while the other fractions (Cs/Sr, Zr/Mo, Tc, REE) should be incorporated into glass. Furthermore, the Cs/Sr fraction can also be separated, and Cs and Sr radionuclides can be used to obtain ionizing radiation sources.[20]

To immobilize both actinide, REE–actinide HLRW fractions and individual actinides (Np, Pu, Am, Cm), matrices have been developed based on stabilized zirconium dioxide (tazheranite/fianit), stabilized titanate, zirconate and mixed pyrochlore, murataite, zirconolite, perovskite, garnet, apatite/britholite, monazite, kosnarite, *etc*. They possess very high radiation and chemical stability.[5,7,21,22] Some of them (tazheranite/fianit, pyrochlore, murataite, zirconolite, garnet, *etc*.) melt congruently and can be obtained by crystallization from a melt, including the cold pot process.[23–25]

Due to the relatively small amounts of the fraction containing minor actinides, it is not necessary to build high-capacity solidification units. It is best to implement these processes on industrial scale using small IMCP plants with a throughput of up to 10 kg h$^{-1}$ (ref. 26) or self-propagating high-temperature synthesis (SHS) units.[27]

Currently, new matrix materials and plants for vitrification of HLRW from reprocessing of SNF that were not processed before (AMB reactor, nitride fuel, transportation facilities, research reactors), HLRW from past defense activities,[28] HLRW from pyroelectrochemical treatment of SNF,[29] from operational RW of nuclear plants,[30] actinide-containing ashes and sludge,[31] and institutional intermediate-level radioactive wastes (ILRW)[32] are under the development. Particular attention is paid to glass-crystalline materials, since they can be obtained in melters of the same type as those used in vitrification of HLRW and ILRW, and HLRW components can be distributed between the glass and crystalline phase in the resulting materials, thus providing an optimum distribution of radionuclides based on their crystallochemical behaviour.[33]

**SNF reprocessing.** The further development of nuclear power industry depends on the solution of problems related to a safe operation of nuclear fuel cycle plants, formation, storage and disposal of RW and minimization of their volume. At this stage, the main directions of radiochemical studies include new scientific and technological approaches to the preparation and treatment of SNF, solution of HRW management , including transmutation of long-lived actinide isotopes and studies on the main regularities of the behaviour of man-made radionuclides in the environment.

It also seems extremely important to study the feasibility of using the thorium–uranium fuel cycle (homogeneous thorium nuclear reactor on fluoride salt melts) in nuclear power industry.[34] The main efforts of scientists and engineers in many countries of the world aim at solving these problems.

The currently used technology for reprocessing of SNF from nuclear power plants is based on the PUREX process, an aqueous chemical method using a 30% solution of tri-*n*-butyl phosphate (TBP) as the extracting agent for retrieval and refinement of fissile materials.[35] This process produces up to 7–12 tons of highly acidic aqueous and toxic organic waste solutions per 1 ton of SNF that require further management and disposal.[36] Despite the considerable improvements in various stages of the PUREX process that make it more cost effective and efficient,[37] creation of a new up-to-date ecologically acceptable, safe and efficient technology for SNF treatment remains a highly urgent task. It has been shown[38] that, in contrast to the PUREX process using aggressive and environmentally hazardous strong nitrate acidic solutions for dissolution of SNF, it may be easily dissolved in diluted acidic solutions ($[H^+]$ ~ 0.1 M) of $Fe^{III}$ nitrate with separation of uranium and plutonium from FP. Other technologies for SNF management from nuclear power plants are also under the development in Russia: the 'CARBEX process' (from 'carbonate extraction') based on the use of carbonate aqueous solutions containing hydrogen peroxide as the oxidant at the stage of transfer of the fuel composition to a carbonate solution followed by extractive isolation and refining of $U^{VI}$ and $Pu^{VI}$ by quaternary ammonium carbonates;[39] extraction with supercritical $CO_2$ with nitric acid–TBP solvates;[40] REMIX (regenerated mixture of U, Pu oxides) process, repeated use of a regenerated uranium–plutonium mixture after enrichment with uranium-235 isotope in thermal-neutron reactors.[41]

A strategy for development of a closed NFC based on fast neutron reactors with sodium or lead heat carrier is considered in Russia.[42] Mixed uranium–plutonium nitride fuel is unified for both types of reactors. Its qualitative characteristics, such as effective density in a fuel element, maximum acceptable temperature of operation, compatibility with the cladding materials and heat carrier, *etc.* are superior to those of MOX fuel, carbide and metallic fuels. Studies on dissolution of simulated nitride SNF in nitric acid did not reveal any serious issues in its hydrometallurgical treatment,[43] let alone in pyrochemical treatment that is carried out in an inert atmosphere.

Hydrometallurgical treatment of SNF from fast neutron reactors at high fuel burn-up and small exposure times involves problems related to precipitates deposition at high FP contents.[44] For this reason, non-aqueous methods of SNF treatment are considered.[42,45] They are characterized as compact, radiation-resistant and low-waste generation methods. A combination of pyroelectrochemical head operations and hydrometallurgical refining, which is described in detail in a number of papers,[42,46] was suggested for the treatment of spent nitride fuel.

Development of new advanced methods for the production of nuclear fuel, including mixed U–Pu fuel, remains a pressing issue, since the existing technologies involve many stages, are time-consuming, consume a lot of electric power and are ecologically harmful. Lately, scientific bases of a simple and efficient method for the preparation of nuclear fuel based on uranium dioxide have been developed at GEOKhI RAS. This method uses microwave radiation for thermal decomposition of uranium compounds (precursors) in a reducing atmosphere.[47] It has also been shown that the use of microwave radiation allows conversion of off-spec ceramic pellets of $UO_2$ to $U_3O_8$ powder in air; the physicochemical properties of the resulting powder are suitable for re-production of nuclear fuel.[48]

A simple, efficient, and relatively low-temperature method for the production of MOX fuel for fast reactors directly from nitric solution was developed for the first time.[49] It was shown that heating of nitric acid solutions of U or U and Pu by microwave radiation in the presence of hydrazine hydrate solution gave their hydrated dioxides that were converted into crystalline dioxides at 300 °C.[49,50] To refine the key processing stages of a promising technologies for SNF processing and to obtain practical experience in reducing the amount of liquid process RW and non-process RW, a pilot demonstration center (PDC) is being created in Russia. It will combine a pilot unit with an annual productivity of no less than 100 tons, with full cycle of SNF processing by 'Simplified PUREX process' technology,[35] a number of research chambers for refinement of innovative processes and technologies, and a storage of vitrified HLRW. The PDC is located on the site of Krasnoyarsk Mining and Chemical Combine (KMCC) (Zheleznogorsk city, Krasnoyarsk Krai).

**Artificial radionuclides in the environment**

Intense development of nuclear technologies of both military and civil purpose in the XX century resulted in entry of radionuclides to the environment.

**Man-made radionuclides sources in the environment.** NFC enterprises are currently the main existing and potential sources of man-made radionuclides in the environment, including each of their stages, starting from mining and milling of uranium ore and up to the final stage that involves RW storage and disposal.

Depending on the sources and pathways of entry and propagation of man-made radionuclides, both global and local (regional) environment pollution by these substances occurs. The major global sources of man-made radionuclides were nuclear weapons tests in the atmosphere and on the Earth surface, as well as major accidents at nuclear power plants in Chernobyl and Fukushima. Local sources of radionuclides include NFC enterprises, particularly radiochemical complexes for SNF treatment, underground nuclear explosions, including 'peaceful' ones, as well as RW storage and disposal sites. Figure 2 shows a comparison of the amount of radionuclides that enter the environment from various sources.[51] It is evident from the Figure 2 that the main sources of entry of man-made radionuclides to the environment include previous nuclear explosions in the atmosphere and activities of radiochemical complexes for SNF treatment (PA 'Mayak' and the facility in Hanford).

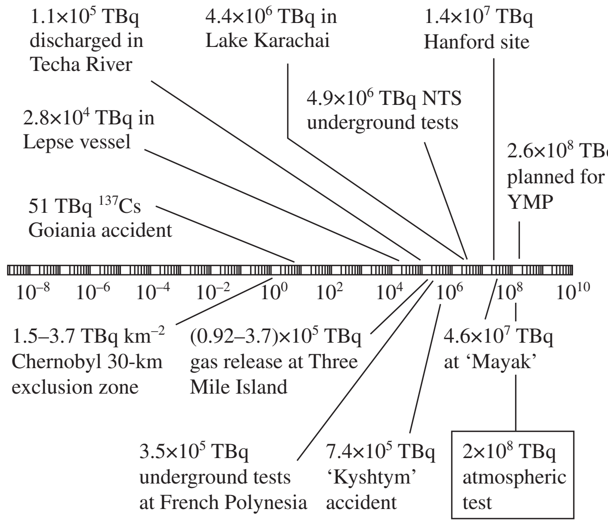


**Figure 2** Major sources of man-made radionuclides in the environment. Figure from ref. 51 © 2010 Elsevier. Reproduced with permission.

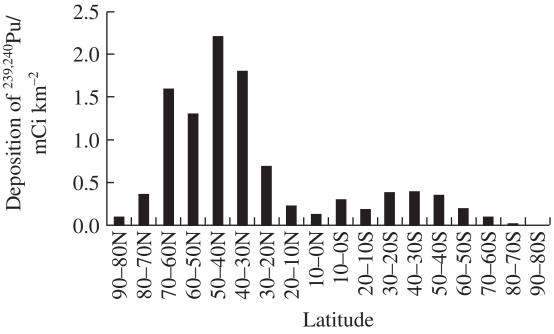


**Figure 3** Latitudinal distribution of $^{239,240}$Pu fallouts due to nuclear weapon tests in the atmosphere.

Global fallouts of radionuclides after nuclear weapon tests have affected the entire Earth surface. The fallout of plutonium-239,240 in the Northern hemisphere amounts to 256±33 kCi, which is much more than in the Southern hemisphere (69±14 kCi).[52] The latitudinal distribution of global $^{239,240}$Pu fallouts after nuclear explosions is shown in Figure 3 (data are taken from ref. 52). The plutonium content in various countries of the Northern hemisphere varies within 50–150 Bq m$^{-2}$.

Crashes of satellites with nuclear power units also resulted in global pollution with radionuclides, *e.g.*, $^{238}$Pu. In fact, destruction of American satellite SNAP-9A containing 1 kg of $^{238}$Pu onboard in top atmosphere layers of the Southern hemisphere resulted in fallout of 10.8 kCi $^{238}$Pu, which is ten times more than the total $^{238}$Pu fallout due to nuclear weapon tests.[52]

As a result of the Chernobyl NPP accident in 1986, about 5300 PBq of various radionuclides entered the environment, including 4–10 PBq of $^{90}$Sr, 85–98 PBq of $^{137}$Cs, 0.015–0.03 PBq of $^{238}$Pu, 0.013 PBq of $^{239}$Pu and 0.018 PBq of $^{240}$Pu, not to mention radioactive isotopes of noble gases.[53]

**Table 2** Estimated release of radionuclides to the atmosphere due to the accident at Fukushima Daiichi NPP.[54,55]

| Radio-nuclide | $T_{1/2}$ | Total content in fuel/Bq | Amount that entered the atmosphere/Bq | Fraction that entered the atmosphere |
|---|---|---|---|---|
| $^{85}$Kr | 10.7 years | 8.37×10$^{16}$ | | 100 |
| $^{89}$Sr | 10.5 days | 5.93×10$^{18}$ | 1.96×10$^{15}$ | 0.033 |
| $^{90}$Sr | 28.7 years | 5.22×10$^{17}$ | 1.39×10$^{14}$ | 0.027 |
| $^{99}$Mo | 65.9 h | 1.14×10$^{19}$ | 6.70×10$^{9}$ | |
| $^{99m}$Tc | 6.01 h | 9.98×10$^{18}$ | | |
| $^{110m}$Ag | 249.8 days | 1.64×10$^{16}$ | | |
| $^{125}$Sb | 2.76 years | 4.31×10$^{16}$ | | |
| $^{129m}$Te | 33.6 days | 1.89×10$^{17}$ | 3.33×10$^{15}$ | 1.8 |
| $^{131}$I | 8.02 days | 6.01×10$^{18}$ | 1.59×10$^{17}$ | 2.6 |
| $^{132}$Te | 3.2 days | 8.69×10$^{18}$ | 8.84×10$^{16}$ | 1.0 |
| $^{133}$I | 20.8 days | 5.27×10$^{17}$ | 4.22×10$^{16}$ | 8.0 |
| $^{133}$Xe | 5.24 days | 1.20×10$^{19}$ | | 100 |
| $^{134}$Cs | 2.06 years | 7.19×10$^{17}$ | 1.75×10$^{16}$ | 2.4 |
| $^{136}$Cs | 13.2 days | 2.18×10$^{17}$ | | |
| $^{137}$Cs | 30 years | 7.00×10$^{17}$ | 1.53×10$^{16}$ | 2.2 |
| $^{144}$Ce | 284.9 days | 5.92×10$^{18}$ | 1.15×10$^{13}$ | 0.00019 |
| $^{238}$Pu | 87.7 years | 1.47×10$^{16}$ | 1.88×10$^{10}$ | 0.00013 |
| $^{239}$Pu | 24100 years | 2.62×10$^{15}$ | 3.23×10$^{9}$ | 0.00012 |
| $^{240}$Pu | 6570 years | 3.27×10$^{15}$ | 3.13×10$^{9}$ | 0.00010 |
| $^{241}$Pu | 13.2 years | | 1.25×10$^{12}$ | |
| $^{241}$Am | 433 years | 1.55×10$^{15}$ | | |
| $^{242}$Cm | 162.8 days | 2.83×10$^{17}$ | 1.02×10$^{11}$ | 0.00004 |
| $^{244}$Cm | 18.11 years | 8.64×10$^{15}$ | | |
| $^{54}$Mn | 312.1 days | 2.83×10$^{14}$ | | |
| $^{60}$Co | 5.27 years | 9.42×10$^{12}$ | | |

The conditions of development of the accident at Fukushima Daiichi NPP in 2011 with melting of the active zone and accordingly its effect on the environment differ considerably from the Chernobyl accident.[51] Highly volatile radionuclides were the major environment pollution factor due to this accident (Table 2). As concerns plutonium, its content in the 20-km exclusion zone did not exceed significantly the mean levels typical of global fallouts.[51]

Territories around NFC radiochemical facilities are examples of local environment pollution. PA 'Mayak' is the largest radiochemical plant in Russia founded in 1948 for the production of weapons-grade plutonium. During PA 'Mayak' operation, rather a complex ecological situation formed in its territory due to a series of accidents in the plants (*e.g.*, the accident in 1957) and RW disposal to open-surface water bodies in the 1950–1970s.[56] The most polluted water bodies are B-9 (Karachay lake) and B-17 (Staroe Boloto). According to the investigation in 2002, the total of components in the open part of B-9 water body (water, silts, floor clay loam) contain 30 MCi of β-emitters and 1 MCi of α-emitters, including plutonium.[57] The major fraction of radionuclides is contained in silts and clay loams of the lake floor. The content of $^{239,240}$Pu in the silts of these water bodies is around 10$^{7}$–10$^{8}$ Bq kg$^{-1}$ of dry mass.[57] It is expected that the B-9 water body will be completely 'conserved' in 2015, *i.e.* its surface will be covered by concrete blocks.

The so-called once-through reactors had been operating for a long time at the KMCC. As a result, radionuclides entered the ecosystem of Yenisei river, where they mostly accumulated in bottom sediments and in riverside soils.[58] The vertical distribution of plutonium in riverside soils is quite nonuniform, presumably due to both the nonuniform influx of radionuclides and variable deposition rate, as well as post-sedimentation processes. The maximum content of $^{239,240}$Pu in the samples studied by Kuznetsov *et al*.[58] amounts to 17.8 Bq kg$^{-1}$.

The mean content of man-made radionuclides in the biosphere is considerably smaller than that of $^{40}$K and radionuclides of the $^{238}$U and $^{232}$Th families. This is illustrated by Figure 4 that shows data on the content of $^{137}$Cs which entered the World ocean from various sources in comparison with the total content of natural radionuclides $^{40}$K and $^{238}$U.[55]

It is evident from Figure 5 (data are taken from ref. 59) that the overall contribution of man-made radionuclides that have entered the biosphere to the total radiation exposure of the population is insignificant and amounts to ~1% from NFC plants.

Data on the content and accumulation of man-made radionuclides are extremely important for estimating the effect of these nuclides on the population and biosphere and for forecasting the trends of radiation situation, as well as for activities on remediation of contaminated territories. These are the key data

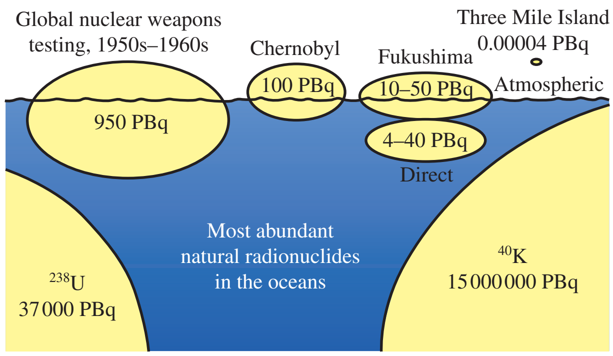


**Figure 4** Comparison of $^{137}$Cs entry (PBq) to the World ocean from various sources with the content of natural radionuclides $^{40}$K and $^{238}$U. Figure from ref. 55 © 2014 The Oceanography Society. Reproduced with permission.

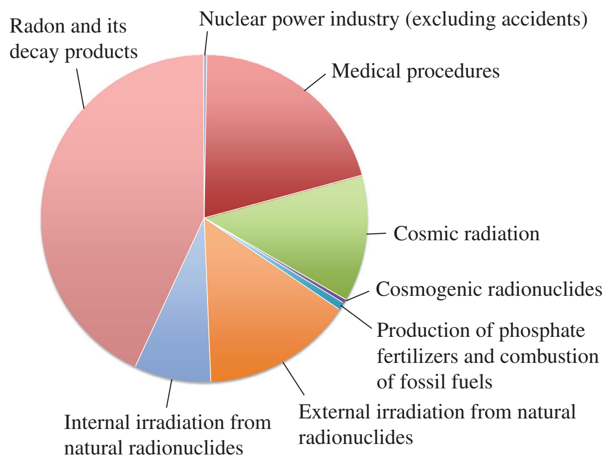


**Figure 5** Contribution of various irradiation sources to the radiation exposure of the population (on average throughout the Earth).

for building prognostic models of the migration behaviour of radionuclides and for development of methods for remediation of territories previously contaminated by radionuclides.

**Source-dependent speciation and behaviour of radionuclides.** Determination of the total amount of radionuclides in various natural objects was performed for a long time. Detailed maps and atlases with pollution levels have been composed for certain regions (*e.g.,* ref. 60). At the same time, the regularities of radionuclide migration, their bioavailability and hence potential hazard for the biosphere is largely determined by their source-dependent speciation and physicochemical properties, not just by local geochemical conditions.[61,62]

As noted above, various radionuclides are formed in nuclear explosions and due to operation of NFC plants. Among these, actinide isotopes are the most radiotoxic and extremely hazardous. In fact, unlike other radionuclides, a feature of actinides, and plutonium in particular, is that they are capable of forming extremely low-soluble crystalline micron- and submicron-sized radioactive particles – ‘hot’ particles – at high temperatures. Therefore, nuclear explosions,[63] accidents with melting of the active reactor zone,[64,65] fires,[66] use of ammunitions containing depleted uranium[67,68] and other high-temperature activities result in plutonium entry in the form of ‘hot’ particles. The behaviour of ‘hot’ particles in the environment is determined by the conditions of their formation, *i.e.*, temperature, presence of oxygen and other elements and other factors, while their dissolution rate is largely determined by the size and morphology of the particles themselves. Thus, radionuclides in ‘hot’ particles are present in extremely kinetically stable physicochemical forms that are not in thermodynamic equilibrium with the environment.

Batuk *et al*.[61] were the first to perform a detailed study and generalize data on the speciation of actinides in the samples taken at various contaminated territories, *viz*., soils, grounds and bottom sediments near Chernobyl NPP, nuclear complexes at Hanford (USA), Rocky Flats (USA), PA ‘Mayak’ (Russia), and in the territory of McGuire AFB (USA). It has been shown by synchrotron radiation methods (X-ray powder diffraction, XANES, EXAFS, XRF) that the prehistory of the formation of particles plays the major role in the behaviour of radionuclides in the environment. For example, it was found that the bottom sediments of B-17 water body (PA ‘Mayak’) simultaneously contained particles of dissimilar origin within one sample, where uranium was represented both as $UO_{2+x}$, $U_3O_8$ and $U^{VI}$ oxide.

Actinides in soils near the damaged reactor at Chernobyl NPP are represented by ‘hot’ particles of various phases, element and radionuclide compositions.[64] During the accident (explosion) in the presence of metallic zirconium and graphite, various particles formed at temperatures about 2600 °C,[69] where uranium existed in the reduced form as $UO_2$ and solid solutions $UO_2$–$ZrO_2$ with various U/Zr ratios from $(U_{0.985}Zr_{0.015})O_2$ to $(Zr_{0.995}U_{0.005})O_2$. The ‘hot’ particles that arrived in a few subsequent days during the fire contained uranium in higher oxidation states, $UO_{2+x}$. These particles manifested considerably smaller kinetic stability and underwent relatively fast oxidation to give $U^{VI}$ compounds.[65]

The behaviour of ‘hot’ particles in soils depends on the rate of their dissolution with transition of radionuclides to a soluble form.[70] In fact, dissolution of ‘hot’ particles in radioactive wastes buried in the ‘Red forest’ in the vicinity of the 4th power unit of Chernobyl NPP within foliage and upper soil layer resulted in migration of plutonium by 5–15 m during 1987–2005, apparently in the form of low-molecular organic compounds.

The high kinetic stability of ‘hot’ particles is also demonstrated by the fact that they have been present in the bottom sediments of Karachay lake (PA ‘Mayak’) for a long time. Plutonium in these bottom sediments exists in a strongly bound form,[71] as shown in ref. 72 where plutonium-containing particles were found which, apart from Pu and O, also contained Si, Al, Mg, Fe, P and Cl.

Similar data were obtained for the bottom sediments and riverside soils of Yenisei river near the KMCC. It has been shown by sequential extraction technique that plutonium has low mobility in most cases. It exists in residual hardly soluble fractions, apparently due to the presence of plutonium-containing ‘hot’ particles.[73,74] This is confirmed in the study by Skipperud *et al*.[75] who determined the forms in which plutonium exists in Yenisei and Ob’ rivers. It was found that the majority of plutonium in the bottom sediments of these rivers exists in fractions soluble in $H_2O_2$ (a mild oxidant) and $HNO_3$ and is incorporated in natural organic compounds, but a part of plutonium exists as ‘hot’ particles in the insoluble residue.

Aside from ‘hot’ particles, another form of entrance of man-made radionuclides, including actinides, to the environment involves their soluble compounds contained in the aqueous effluents of NFC plants. Furthermore, soluble species of radionuclides are formed upon decomposition of ‘hot’ particles. In this case, their behaviour is determined by local geochemical conditions rather than their forms of entry.

The concentration of man-made radionuclides in the environment is low, therefore various methods for their preliminary isolation and concentrating before quantitative determination are used. Numerous publications describe the pre-concentration of radionuclides from aqueous media.[76,77] Most commonly, co-precipitation and sorption methods are used for these purposes, with inorganic[78,79] and polymeric sorbents containing various complexing groups,[80,81] including fibrous filled sorbents.[82,83] Here, we will focus on new methods and sorption materials being developed.

Lately, carbon nanomaterials (CNM), *i.e*., graphene oxide, carbon nanotubes, nanodiamonds, *etc*., have been used for pre-concentration of radionuclides. Prospects of CNM application for solution of the most important problems in radiochemistry and radioecological safety are noted, such as cleaning of aqueous media, recovery of radionuclides from complex solutions, solidification of highly radioactive waste and other NFC problems.[84,85]

The considerable interest in CNM is due to the development of inexpensive and effective methods of their preparation.[85] The sorption capability of CNM toward radionuclides is determined by the presence of diverse oxygen-containing groups on their surfaces, including epoxy, carboxy, hydroxy and carbonyl groups. CNMs are characterized by large free specific surfaces. In fact, the specific free surface of graphene oxide, which has the structure of oxidized graphene sheets with a thickness of one atomic layer, can reach a few thousand $m^2 g^{-1}$.[86] The large free specific

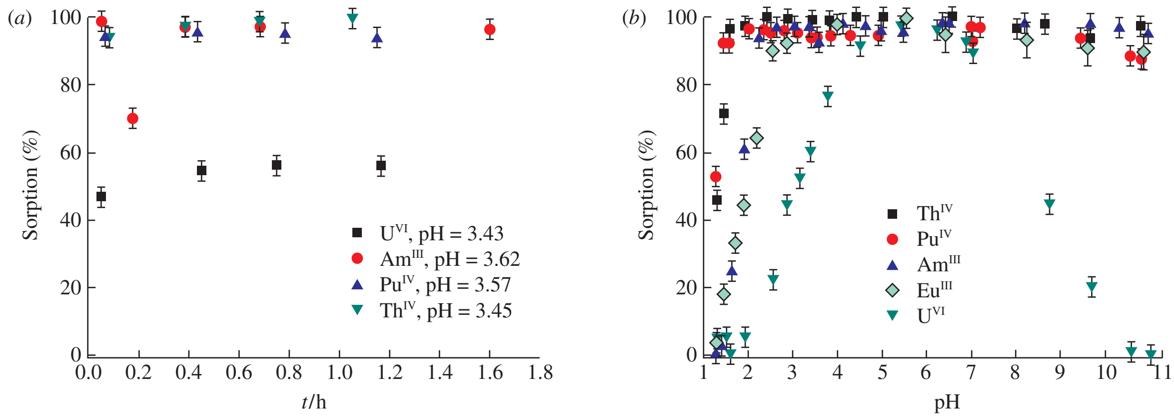


**Figure 6** (*a*) Adsorption kinetics of actinide ions on graphene oxide and (*b*) dependence of sorption on pH. Figure from ref. 86 © 2013 The PCCP Owner Societies. Reproduced with permission.

surface determines the fast sorption kinetics and large distribution coefficients of radionuclides (>$10^6$ ml $g^{-1}$) for such 'hard' cations as actinide and lanthanide ions.[87] Figure 6 presents data on the sorption kinetics of actinide ions from aqueous solutions and dependences of sorption on pH. It follows from these data that dynamic equilibrium is reached rather quickly and quantitative isolation occurs at pH > 2 for $Th^{IV}$ and $Pu^{IV}$, at pH > 3 for $Eu^{III}$ and $Am^{III}$ and at pH > 4 for $U^{VI}$. This determines the prospects of using these sorbents for analyzing environment objects for the content of radionuclides.

An important property of graphene oxide is that it is capable of coagulation with an increase in the solution ionic strength, the critical concentration of coagulation depends on their charge and hardness. Coagulation can be explained by 'glueing together' of separate sheets due to interaction with the metal cations located between them.[85]

Of the other CNMs, practical application was found by carbon nanotubes (CNT).[84,87,88] For example, the use of multiwall CNT treated with an acid for recovery of certain radionuclides was described ($^{239}Pu^{IV}$,[89] $^{243}Am^{III}$,[90] $Th^{IV}$,[91] $^{152–154}Eu$[92]). The maximum recovery of Eu and Am is attained at pH ⩾ 6 and that of thorium is attained at pH ⩾ 4. The recovery ratios of americium and europium nearly do not depend on the solution ionic strength, which indicates that sorption of radionuclides occurs due to complexation with functionally active groups of oxidized CNT. It appears particularly promising to use CNT as matrices in solid-phase extraction. By modifying CNT with selective organic reagents, it becomes possible to improve their selectivity towards specific radionuclides and to use them in a broad acidity range.[93] Composite sorbents were obtained at GEOKhI RAS[94,95] by impregnation of CNT with various ligands, *e.g.*, diphenyl(dibutylcarbamoylmethyl)phosphine oxide ($Ph_2Bu_2CMPO$) and tri-*n*-octylphosphine oxide (TOPO), as well as with phosphonium ionic liquid Cyphos IL-101. The resulting sorbents possess good kinetic properties and efficiency toward actinide ions.

In studies on the behaviour of man-made radionuclides in the environment, especially in estimation of their effects, the most attention is paid to the behaviour of $^{239,240}Pu$ isotopes that are the most hazardous to the environment, as well as $^{137}Cs$ and $^{90}Sr$ that are relatively long-lived radionuclides formed in high yields in nuclear fission. The behaviour of plutonium in the environment is determined by numerous factors, primarily the possibility of its existence in oxidation states three, four, five and six, which determines the diversity of its chemical species. Data on the oxidation states of plutonium and its cationic and anionic forms in natural waters as functions of pH and Eh are shown in Figure 7.

Thus, the possibility of plutonium existence in various oxidation states and forms determines the peculiarities of its behaviour in sorption on soil and rock components, on colloid particles and

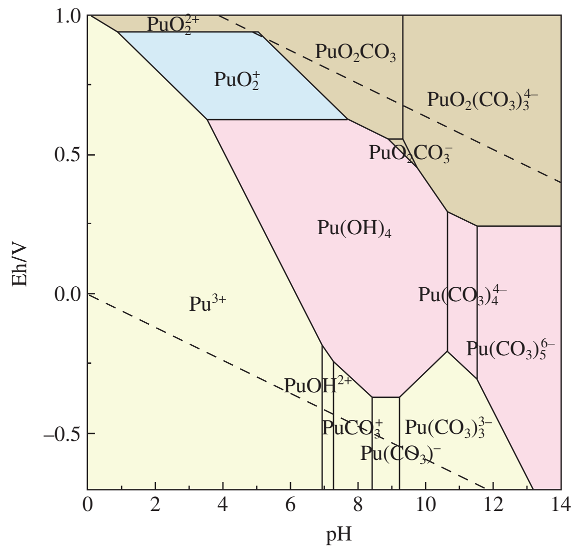


**Figure 7** Pourbaix diagram for plutonium ([Pu] = $1\times10^{-12}$ mol $dm^{-3}$, $\lg p_{CO_2} = -3.5$).

microorganisms, complexation reactions in solutions with natural ligands (carbonate and chloride anions, humic substances *etc.*), as well as formation of poorly soluble compounds. A possible scheme of plutonium behaviour in the environment is shown in Figure 8.[96,97]

The tetravalent state is the dominating oxidation state of plutonium in the environment, where it manifests high reactivity

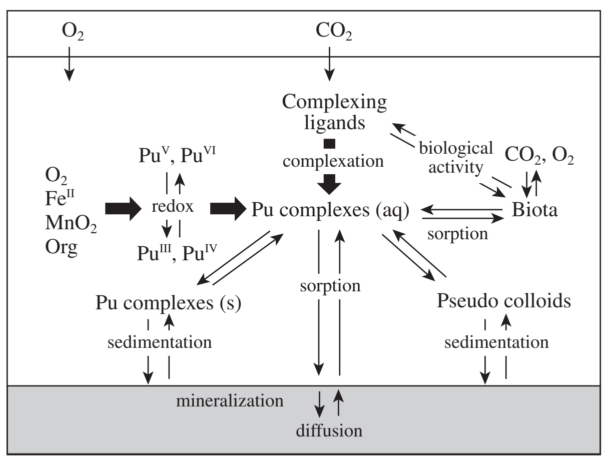


**Figure 8** Simplified scheme of biogeochemical behaviour of plutonium in the environment. Figure from ref. 96 © 2001 Elsevier. Reproduced with permission.

in various reactions, including formation of poorly soluble compounds, hydrolysis, complexation in solutions, sorption on metal oxides and hydroxides. It was therefore believed that plutonium had extremely low migration mobility in the environment due to the formation of extremely poorly soluble compounds and sorption on soils and rocks. On the other hand, the high liability of plutonium to sorption on particles of oxides or oxyhydroxides of iron, manganese, titanium and other elements present in natural waters to give pseudo-colloid particles governs its fast migration.[98,99] In fact, plutonium was detected in subsoil waters from observation wells at Nevada Test Site, USA.[98,100] Using the isotope ratios of plutonium, the nuclear explosion performed at a distance of 1.3 km was identified as its source. Over 95% of plutonium contained in ground waters was bound to colloid particles consisting of clays and zeolites.

The first direct proof of the existence of pseudocolloidal plutonium particles was obtained in a study of subsoil waters samples taken in the vicinity of Karachay lake. It was found by secondary ion mass spectrometry with nanometer resolution and by high-resolution transmission electron microscopy (HRTEM)[99] that plutonium was mostly bound with colloid particles of amorphous ferrihydrite and $MnO_2$ (Figure 9) that determined its migration over long distances.

The presence of plutonium on poorly soluble colloid particles of amorphous iron oxides is confirmed by by successive treatments[101] of colloid particles isolated from groundwater of Karachay contaminated aureole. Colloid particles containing plutonium were also found in silt and in bottom sediments.[102] It has been shown that plutonium is strongly retained by silts on washing

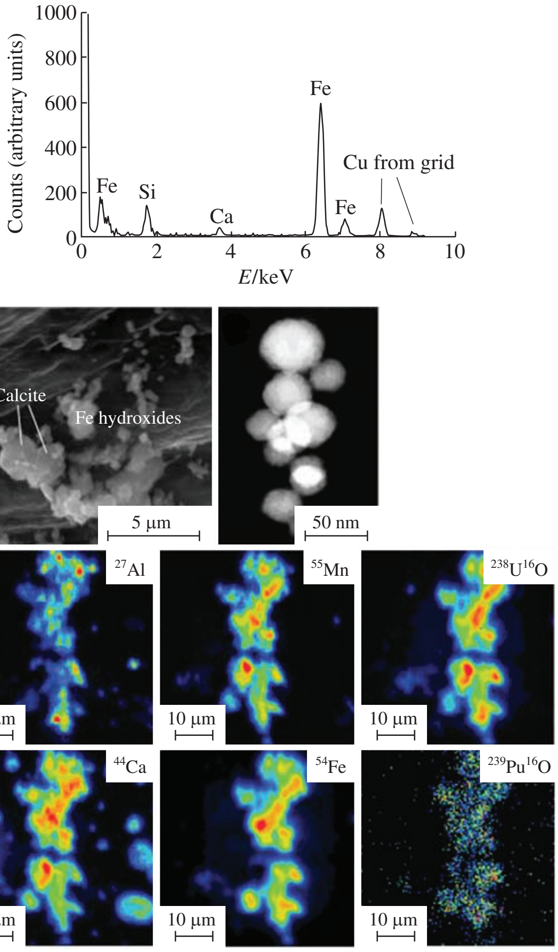


**Figure 9** Images and elemental maps obtained by HRTEM and secondary-ion mass spectrometry with nanoscale resolution for plutonium-containing colloid particles from groundwater samples collected around Karachay Lake. Figure from ref. 99 © 2006 AAAS. Reproduced with permission.

with natural groundwater and with water enriched by sodium nitrate. However, colloid particles with sizes more than 10 nm passed into the solution in the latter case.

Miller *et al.*[103] formulated the criteria that determine the colloid transport of radionuclides, including plutonium, as a significant mechanism of their migration: (1) colloids should be present, (2) they should be mobile, (3) they should be stable, (4) they should trap radionuclides, (5) this trapping should be irreversible.

A more detailed study of the formation mechanisms of colloid particles containing plutonium by such advanced methods as HRTEM and X-ray absorption spectroscopy (XANES and EXAFS) has shown that sorption of plutonium on various oxides is accompanied by redox reaction and formation of oxide nanoparticles.[104–111]

The mechanism of occurring processes has been studied for sorption of plutonium on goethite ($\alpha$-FeOOH),[104,105] magnetite ($Fe_3O_4$),[106,107] pyrolusite,[108] manganite (MnOOH), hausmannite ($Mn_3O_4$)[109] and $Mn^{III}$-substituted goethite[110] as examples. Stabilization of $Pu^{IV}$ on particle surfaces results in the formation of oxide nanoparticles with various compositions. In fact, Powell *et al.*[111] showed that 2–5 nm particles containing plutonium were formed upon addition of a $Pu^{IV}$ solution to goethite and quartz suspensions. It was found that in the case of goethite, $Pu_4O_7$ nanoparticles were formed on the surface. The mechanism of their formation was explained by epitaxial growth due to similarity between the lattice parameters. The resulting particles are stable for a few months both at 25 and 80 °C and are not converted to $PuO_2$.[112] As shown by Romanchuk,[113] kinetically stable nanoparticles with $PuO_{2+x}{\cdot}nH_2O$ composition are formed upon plutonium sorption on hematite even at concentrations of ~$10^{-10}$ mol $dm^{-3}$.[107]

Additional requirements and data from new approaches and methods are required to obtain a more comprehensive understanding of the migration mechanism in the environment for plutonium and other radionuclides.

## Conclusion

Based on the above data, one can conclude that further development of nuclear power industry is related to ensuring its ecological safety. It primarily requires the RW management problem to be solved (reduction of the volume, development of new mineral-like matrices, study of their properties and methods for incorporation of radionuclides into these matrices, as well as methods and techniques for transmutation of long-lived radionuclides), existing nuclear fuel production and SNF reprocessing technologies to be improved and new ones to be created. Reliable estimation of the effects of NPPs and NFC plants on the environment requires new selective and efficient methods for pre-concentration of radionuclides to be created, along with high sensitivity methods for determination of their content and speciation in environment, and models for reliable forecasting of their behaviour to be developed.

## References


1 V. I. Vernadsky, *Ocherki i rechi (Sketchs and Speeches)*, NKhTI, Petrograd, 1922, pp. 1, 37 (in Russian).
2 B. F. Myasoedov, *Ross. Khim. Zh.*, 1996, **40**, no. 6, 13 (in Russian).
3 *IAEA Annual Report 2013*, GC(58)/3, IAEA, Vienna, 2014.
4 M. Ceyhan and J. S. Lee, *Proceedings of the International Conference on Management of Spent Fuel from Power Reactors*, IAEA, Vienna, 2006, p. 1.
5 *Pererabotka Yadernogo Goryuchego (Reprocessing of the Spent Fuel)*, eds. S. Stoler and R. Richards, Moscow, Atomizdat, 1964, p. 184 (in Russian).
6 K. Nash, in *Recent Advances in Actinide Sciences*, eds. R. Alvarez and N. D. Bryan, RSC Publishing, Cambridge, 2006, p. 427.
7 S. V. Stefanovsky, S. V. Yudintsev, R. Giere and G. R. Lumpkin, *Nuclear Waste Forms. Energy, Waste and the Environment: A Geological Perspective*, Geological Society, Special Publication, London, 2004, vol. 236, p. 37.

8 S. V. Yudintsev, S. V. Stefanovsky and R. C. Ewing, in *Structural Chemistry of Inorganic Actinide Compounds*, eds. S. V. Krivovichev, P. C. Burns and I. G. Tananaev, Elsevier, Amsterdam, 2007, pp. 457–490.

9 W. J. Weber, R. C. Ewing, C. A. Angell, G. W. Arnold, A. N. Cormack, J. M. Delaye, D. L. Griscom, L. W. Hobbs, A. Navrotsky, D. L. Price, A. M. Stoneham and M. C. Weinberg, *J. Mater. Res.*, 1997, **12**, 1946.

10 I. W. Donald, *Waste Immobilization in Glass and Ceramic Based Hosts: Radioactive, Toxic and Hazardous Wastes*, Wiley, Chichester, 2010, vol. XVII.

11 A. E. Ringwood, S. E. Kesson, K. D. Reeve, D. M. Levins and E. J. Ramm, in *Radioactive Waste Forms for the Future*, eds. W. Lutze and R. C. Ewing, North-Holland, Amsterdam, 1988, p. 233.

12 R. Vance, M. W. A. Stewart and S. A. Moricca, *J. Aust. Ceram. Soc.*, 2014, **50**, 38.

13 A. S. Wagh, *Chemically Bonded Phosphate Ceramics – Twenty-First Century Materials with Diverse Applications*, Elsevier, Oxford, 2004, ch. 17.

14 S. E. Vinokurov, Yu. M. Kulyako, A. S. Wagh and B. F. Myasoedov, *Proceedings of the Conference of Knowledge-based Materials and Technologies for Sustainable Chemistry*, Tallinn, 2005, p. 124.

15 Yu. M. Kulyako, S. E. Vinokurov and B. F. Myasoedov, in *Recent Advances in Actinide Sciences*, eds. R. Alvarez and N. D. Bryan, RSC Rublishing, Cambridge, 2006, p. 427.

16 S. E. Vinokurov, Yu. M. Kulyako and B. F. Myasoedov, *Ross. Khim. Zh.*, 2010, **54**, no. 3, 81 (in Russian).

17 D. Singh, V. R. Mandalika, S. R. Parulekar and A. S. Wagh, *J. Nucl. Mater*., 2006, **348**, 272.

18 A. Aloy, E. Kovarskaya and T. Koltsova, *International Conference on Future Nuclear Systems ‘Global-99’*, Jackson Hole, Wyoming, USA (CD version).

19 S. E. Vinokurov, Yu. M. Kulyako, B. F. Myasoedov and M. D. Samsonov, *RF Patent*, 2381580, 2008.

20 A. S. Aloy, S. V. Baranov, M. V. Logunov, O. M. Slunichev, A. G. Kharlova and L. G. Tsaritsyna, *Istochniki gamma-izlucheniya s tseziem-137. Svoistva, proizvodstvo, primenenie (Sources of Gamma-radiation with Cesium-137. Properties, Production and Applications)*, PA ‘Mayak’, Ozersk, 2013, p. 232 (in Russian).

21 S. V. Stefanovsky, A. A. Zherebtsov and S. A. Dmitriev, *Fizika i Khimiya Obrabotki Materialov*, 2014, no. 3, 44 (in Russian).

22 S. V. Stefanovsky, S. V. Yudintsev and B. F. Myasoedov, *Dokl. Chem.*, 2012, **447**, 296 (*Dokl. Akad. Nauk*, 2012, **447**, 644).

23 S. V. Stefanovsky, V. V. Lebedev, A. G. Ptashkin, S. A. Dmitriev and J. C. Marra, *Adv. Sci. Technol.*, 2010, **73**, 183.

24 I. A. Sobolev, B. F. Myasoedov, S. V. Stefanovsky, S. V. Yudintsev and Yu. M. Kulyako, *Radiochemistry*, 2001, **43**, 124 (*Radiokhimiya*, 2001, **43**, 113).

25 S. V. Stefanovsky, A. G. Ptashkin, O. A. Knyazev, M. S. Zenkovskaya, O. I. Stefanovskaya, G. A. Varlakova, O. A. Burlaka, S. V. Yudintsev and B. S. Nikonov, *Fizika i Khimiya Obrabotki Materialov*, 2008, no. 4, 18 (in Russian).

26 S. V. Stefanovsky, I. A. Knyazev, B. F. Myasoedov, B. S. Nikonov and S. V. Yudintsev, *Fizika i Khimiya Obrabotki Materialov*, 2013, no. 3, 70 (in Russian).

27 E. M. Glagovsky, S. V. Yudintsev, A. V. Kuprin, L. P. Pelevin, E. E. Konovalov, V. I. Velichkin and B. F. Myasoedov, *Radiochemistry*, 2001, **43**, 632 (*Radiokhimiya*, 2001, **43**, 557).

28 M. B. Remizov, P. V. Kozlov, M. V. Logunov, V. K. Koltyshev and K. K. Korchenkin, *Voprosy Radiatsionnoi Bezopasnosti*, 2014, **3**, 17 (in Russian).

29 Yu. G. Lavrinovich and A. V. Bychkov, *Obrashchenie s otkhodami nevodnykh metodov pererabotki otrabotavshego yadernogo topliva (Management of Wastes from Non-aqueous Methods of Spent Fuel Reprocessing)*, NIIAR, Dimitrovgrad, 2012, p. 111 (in Russian).

30 I. A. Sobolev, S. A. Dmitriev, F. A. Lifanov, A. P. Kobelev, S. V. Stefanovsky and M. I. Ojovan, *Glass Technol.*, 2005, **1**, 28.

31 G. A. Malinina, O. I. Stefanovsky and S. V. Stefanovsky, *J. Nucl. Mater.*, 2011, **416**, 230.

32 V. V. Lebedev and S. V. Stefanovsky, *Voprosy Radiatsionnoi Bezopasnosti*, 2011, no. 2, 16 (in Russian).

33 D. Caurant, P. Loiseau, O. Majérus, V. Aubin-Chevaldonnet, I. Bardez and A. Quintas, in *Glasses, Glass-Ceramics and Ceramics for Immobilization of Highly Radioactive Nuclear Wastes*, Nova Science Publishers, Inc., New York, 2009, p. 445.

34 D. N. Suglobov, R. M. Yakovlev and B. F. Myasoedov, *Radiochemistry*, 2007, **49**, 441 (*Radiokhimiya*, 2007, **49**, 385).

35 Yu. S. Fedorov, B. Ya. Zilberman, A. S. Aloi, E. A. Puzikov, A. Yu. Shadrin and M. Yu. Alyapishev, *Russ. J. Gen. Chem*., 2011, **81**, 1932 (*Ross. Khim. Zh.*, 2010, **54**, no. 3, 12).

36 B. Ya. Zilberman, *Radiochemistry*, 2000, **42**, 1 (*Radiokhimiya*, 2000, **42**, 3).

37 B. Ya. Zilberman, E. A. Puzikov, D. V. Ryabkov, M. N. Makarychev-Mikhaylov, A. Yu. Shadrin, Yu. S. Fedorov and V. A. Simonenko, *Atomnaya Energiya*, 2009, **107**, 273 (in Russian).

38 Yu. M. Kulyako, T. I. Trofimov, E. G. Il’in and B. F. Myasoedov, *Russ. J. Gen. Chem*., 2011, **81**, 1960 (*Ross. Khim. Zh.*, 2010, **54**, no. 3, 35).

39 S. I. Stepanov, A. V. Boyarintsev, M. V. Vazenkov, B. F. Myasoedov, E. O. Nazarov, A. M. Safiulina, I. G. Tananaev, Khen Vin So, A. M. Chekmarev and A. Yu. Tsivadze, *Russ. J. Gen. Chem*., 2011, **81**, 1949 (*Ross. Khim. Zh.*, 2010, **54**, no. 3, 25).

40 T. I. Trofimov, M. D. Samsonov, S. E. Vinokurov, Yu. M. Kulyako and B. F. Myasoedov, *Radiochemistry*, 2014, **56**, 162 (*Radiokhimiya*, 2014, **56**, 139).

41 Yu. S. Fedorov, B. A. Bibichev, B. Ya. Zilberman and A. Yu. Shadrin, *Proceedings of International Conference ‘Global 2009’*, Paris, SNF, 2009, paper #2590.

42 A. Yu. Shadrin, K. N. Dvoeglazov, V. B. Ivanov, V. I. Volk, M. V. Skupov, A. E. Glushenkov, V. M. Troyanov and A. A. Zherebtsov, *Radiochim. Acta*, 2015, **103**, 163.

43 H. Hayashi, H. Sato, H. Shibata, T. Iwai, K. Nishihara and Y. Arai, *Proceedings of the International Conference ‘Global 2011’*, Makuhari, Japan, 2011, paper #392090.

44 F. J. Doucet, D. T. Goddard, C. M. Taylor, I. S. Denniss, S. M. Hutchison and N. D. Bryan, *Phys. Chem. Chem. Phys*., 2002, **4**, 3491.

45 H. Hayashi, T. Sato, H. Shibata, M. Kurata, T. Iwai and Y. Arai, *Science China*, 2014, **57**, 1427.

46 V. I. Volk, A. Yu. Shadrin, S. Veselov, K. N. Dvoeglazov, A. A. Zherebtsov, O. V. Schmidt, V. L. Vidanov, M. V. Kormilitsyn, A. G. Osipenko and S. S. Poglyad, *Proceedings of the International Conference ‘Global 2011’*, Makuhari, Japan, 2011, paper #386756.

47 Yu. M. Kulyako, T. I. Trofimov, M. D. Samsonov, S.A. Perevalov, S. E. Vinokurov, E.G. Ilin and B. F. Myasoedov, *Radiochemistry*, 2011, **53**, 604 (*Radiokhimiya*, 2011, **53**, 509).

48 Yu. M. Kulyako, T. I. Trofimov, M. D. Samsonov, S. E. Vinokurov and B. F. Myasoedov, *Radiochemistry*, 2015, **57**, 127 (*Radiokhimiya*, 2015, **57**, 112).

49 B. F. Myasoedov, Yu. M. Kulyako, A. M. Fedoseev, A. A. Bessonov, T. I. Trofimov, S. A. Perevalov, S. E. Vinokurov, M. D. Samsonov and A. Yu. Shadrin, *Radiochemistry*, 2013, **55**, 574 (*Radiokhimiya*, 2013, **55**, 487).

50 Yu. M. Kulyako, T. I. Trofimov, S. A. Perevalov, D. A. Malikov, S. E. Vinokurov, M. D. Samsonov, B. F. Myasoedov, S. S. Travnikov, K. N. Dvoeglazov and A. Yu. Shadrin, *Radiochemistry*, 2015, **57**, 251 (*Radiokhimiya*, 2015, **57**, 215).

51 Q.-H. Hu, J.-Q. Weng and J.-S. Wang, *J. Environ. Radioact.*, 2010, **101**, 426.

52 E. P. Hardy, P. W. Krey and H. L. Volchok, *Nature*, 1973, **241**, 444.

53 G. Steinhauser, A. Brandl and Th. E. Johnson, *Sci. Total Environ.*, 2014, **470–471**, 800.

54 P. Povinec, K. Hirose and M. Aoyama, *Fukushima Accident: Radioactivity Impact on the Environment*, Elsevier, Amsterdam, 2013.

55 K. O. Buesseler, *Oceanography*, 2014, **27**, 92.

56 B. F. Myasoedov and E. G. Drozhko, *J. Alloys Compd.*, 1998, **271–273**, 216.

57 E. G. Drozhko, P. M. Stukalov, A. I. Aleksakhin, I. A. Ivanov and N. A. Simkina, *Voprosy Radiatsionnoi Bezopasnosti*, 2006, no. 4, 22 (in Russian).

58 Yu. V. Kuznetsov, V. K. Legin, V. N. Strukov, A. P. Novikov, T. A. Goryachenkova, A. E. Shilov and Yu. V. Savitsky, *Radiochemistry*, 2000, **42**, 519 (*Radiokhimiya*, 2000, **42**, 470).

59 J. Hala and J. D. Navratil, *Radioactivity, Ionizing Radiation, and Nuclear Energy*, Konvoj, Czech Republic, 2003.

60 *Atlas zagryazneniya Evropy tseziem posle Chernobyl’skoi avarii (Atlas of the Contamination of Europe by Cesium after the Chernobyl Accident)*, EUROPIAN Communities, EC/EGCE, 1998.

61 O. N. Batuk, S. D. Conradson, O. N. Aleksandrova, H. Boukhalfa, B. E. Burakov, D. L. Clark, K. R. Czerwinski, A. R. Felmy, J. S. Lezama-Pacheco, S. N. Kalmykov, D. A. Moore, B. F. Myasoedov, D. T. Reed, D. D. Reilly, R. C. Roback, I. E. Vlasova, S. M. Webb and M. P. Wilkerson, *Environ. Sci. Technol*., 2015, **49**, 6474.

62 C. C. Wendel, L. Skipperud, O. C. Lind, E. Steinnes, S. Lierhagen and B. Salbu, *J. Radioanal. Nucl. Chem*., 2015, **304**, 1243.

63 C. C. Wendel, L. K. Fifield, D. H. Oughton, O. C. Lind, L. Skipperud, J. Bartnicki, S. G. Tims, S. Hoibraten and B. Salbu, *Environ. Int*., 2013, **59**, 92.

64 S. I. Shabalev, B. E. Burakov and E. B. Anderson, *Mat. Res. Soc. Symp. Proc*., 1997, **465**, 1343.

65 P. Schubert-Bischoff, W. Lutze and B. E. Burakov, *Mat. Res. Soc. Symp. Proc*., 1997, **465**, 1319.
66 V. LoPresti, S. D. Conradson and D. L. Clark, *J. Alloys Compd.*, 2007, **444**, 540.
67 O. C. Lind, B. Salbu, L. Skipperud, K. Janssens, J. Jaroszewicz and W. De Nolf, *J. Environ. Radioact.*, 2009, **100**, 301.
68 P. R. Danesi, A. Markowicz, E. Chinea-Cano, W. Burkart, B. Salbu, D. Donohue, F. Ruedenauer, M. Hedberg, S. Vogt, P. Zahradnik and A. Ciurapinski, *J. Environ. Radioact.*, 2003, **64**, 143.
69 B. E. Burakov, E. B. Anderson, S. I. Shabalev, E. E. Strykanova, S. V. Ushakov, M. Trotabas, J.-Y. Blanc, P. Winter and J. Duco, *Mat. Res. Soc. Symp. Proc*., 1997, **465**, 1297.
70 S. Levchuk, V. Kashparov, I. Maloshtan, V. Yoschenko and N. Van Meir, *Appl. Geochem.*, 2012, **27**, 1339.
71 P. M. Stukalov and N. A. Simkina, *Voprosy Radiatsionnoi Bezopasnosti*, 2008, no. 2, 44 (in Russian).
72 I. E. Vlasova, S. N. Kalmykov, O. N. Batuk, N. V. Kuzmenkova, O. A. Aleksandrova, I. A. Ivanov and I. G. Tananaev, *Voprosy Radiatsionnoi Bezopasnosti*, 2013, no. 2, 48 (in Russian).
73 A. Yu. Bolsunovsky, V. O. Cherkizyan, K. V. Barsykova and B. F. Myasoedov, *Radiochemistry*, 2000, **42**, 620 (*Radiokhimiya*, 2000, **42**, 560).
74 I. E. Vlasova, S. N. Kalmykov, Yu. V. Konevnik, S. G. Simakin, I. S. Simakin, A. Yu. Anokhin and Yu. A. Sapozhnikov, *Radiation Measurements*, 2008, **43**, S303.
75 L. Skipperud, J. Brown, L. K. Fifield, D. H. Oughton and B. Salbu, *J. Environ. Radioact*., 2009, **100**, 290.
76 J. Lehto and X. Hou, *Chemistry and Analysis of Radionuclides: Laboratory Techniques and Methodology*, John Wiley & Sons, New York, 2011, p. 408.
77 *Analysis of Environmental Radionuclides*, ed. P. P. Povinec, Elsevier, Amsterdam, 2008.
78 P. Rajec, L. Matel, J. Orechovska, J. Sucha and I. Novak, *J. Radioanal. Nucl. Chem*., 1996, **208**, 477.
79 M. Galambos, P. Suchanek and O. Rosskopfova, *J. Radioanal. Nucl. Chem*., 2012, **293**, 613.
80 S. Bratskaya, A. Musyanovych, V. Zheleznov, A. Synytska, D. Marinin, F. Simon and V. Avramenko, *ACS Appl. Mater. Interfaces*, 2014, **6**, 16769.
81 J. Kim, H. Lee, J.-W. Yeon, Y. Jung and J. Kim, *J. Radioanal. Nucl. Chem*., 2010, **286**, 129.
82 N. P. Molochnikova, I. G. Tananaev, G. V. Myasoedova and B. F. Myasoedov, *Radiochemistry*, 2007, **49**, 64 (*Radiokhimiya*, 2007, **49**, 58).
83 G. V. Myasoedova, *Ross. Khim. Zh.*, 2005, **49**, no. 2, 72 (in Russian).
84 O. B. Mokhodoeva, D. A. Malikov, N. P. Molochnikova, E. A. Zakharchenko, S. A. Perevalov, G. V. Myasoedova, Yu. M. Kulyako, A. G. Tkachev, S. V. Mishenko and B. F. Myasoedov, *Russ. J. Gen. Chem*., 2011, **81**, 1972 (*Ross. Khim. Zh.*, 2010, **54**, no. 3, 61).
85 F. Belloni, C. Kutahyali, C. C. Rondinella, P. Carbol, T. Wiss and A. Mangione, *Environ. Sci. Technol*., 2009, **43**, 1250.
86 A. Yu. Romanchuk, A. S. Slesarev, S. N. Kalmykov, D. V. Kosynkin and J. M. Tour, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2321.
87 E. G. Rakov, *Russ. Chem. Rev.*, 2001, **70**, 827 (*Usp. Khim.*, 2001, **70**, 934).
88 R. C. Haddon, *Acc. Chem. Res.*, 2002, **35**, 977.
89 S. A. Perevalov and N. P. Molochnikova, *J. Radioanal. Nucl. Chem.*, 2009, **281**, 603.
90 X. Wang, C. Chen, W. Hu, A. Ding, D. Xu and X. Zhou, *Environ. Sci. Technol*., 2005, **39**, 2856.
91 C. L. Chen, X. L. Li and X. K. Wang, *Radiochim. Acta*, 2007, **95**, 261.
92 X. L. Tan, D. Xu, C. L. Chen, X. K. Wang and W. P. Hu, *Radiochim. Acta*, 2008, **96**, 23.
93 E. A. Zakharchenko, D. A. Malikov, N. P. Molochnikova, G. V. Myasoedova and Yu. M. Kulyako, *Radiochemistry*, 2014, **56**, 27 (*Radiokhimiya*, 2014, **56**, 26).
94 E. A. Zakharchenko, D. A. Malikov, G. V. Myasoedova, O. B. Mokhodoeva, N. P. Molochnikova and Yu. M. Kulyako, *Radiochemistry*, 2012, **54**, 159 (*Radiokhimiya*, 2012, **54**, 148).
95 E. Zakharchenko, O. Mokhodoeva, D. Malikov, N. Molochnikova, Yu. Kulyako and G. Myasoedova, *Procedia Chem.*, 2012, **7**, 268.
96 G. R. Choppin and A. Morgenstern, in *Plutonium in the Environment, Radioactivity in the Environment*, ed. A. Kudo, Elsevier, Amsterdam, 2001, p. 91.
97 P. Lindahl, S.-H. Lee, P. Worsfold and M. Keith-Roach, *Marine Environ. Res*., 2010, **69**, 73.
98 A. B. Kersting, D. W. Efurd, D. L. Finnegan, D. L. Rokop, D. K. Smith and J. L. Thompson, *Nature*, 1999, **397**, 56.
99 A. P. Novikov, S. N. Kalmykov, S. Utsunomiya, R. C. Ewing, F. Horreard, A. Merkulov, S. B. Clark, V. V. Tkachev and B. F. Myasoedov, *Science*, 2006, **314**, 638.
100 A. B. Kersting and M. Zavarin, in *Colloid-facilitated Transport of Plutonium at the Nevada Test Site*, eds. S. N. Kalmykov and M. A. Denecke, Springer-Verlag, Berlin, 2011.
101 A. P. Novikov, S. N. Kalmykov, B. F. Myasoedov, I. A. Ivanov and S. I. Rovny, *Voprosy Radiatsionnoi Bezopasnosti*, 2009, no. 1, 12 (in Russian).
102 P. M. Skukalov, A. I. Aleksakhin, I. A. Ivanov and N. A. Simkina, *Voprosy Radiatsionnoi Bezopasnosti*, 2007, no. 1, 3 (in Russian).
103 W. M. Miller, W. R. Alexander, N. A. Chapman, I. G. McKinley and J. A. T. Smellie, *Geological Disposal of Radioactive Wastes and Natural Analogues, Waste Management Series*, Pergamon, Amsterdam, 2000, vol. 2.
104 A. L. Sanchez, J. W. Murray and T. H. Sibley, *Geochim. Cosmochim. Acta*, 1985, **49**, 2297.
105 W. L. Keeney-Kennicutt and J. W. Morse, *Geochim. Cosmochim. Acta*, 1985, **49**, 2577.
106 B. A. Powell, R. A. Fjeld, D. I. Kaplan, J. T. Coates and S. M. Serkiz, *Environ. Sci. Technol*., 2004, **38**, 6016.
107 A. Yu. Romanchuk, S. N. Kalmykov and R. A. Aliev, *Radiochim. Acta*, 2011, **99**, 137.
108 A. Morgenstern and G. R. Choppin, *Radiochim. Acta*, 2002, **90**, 69.
109 D. A. Shaughnessy, H. Nitsche, C. H. Booth, D. K. Shuh, G. A. Waychunas, R. E. Wilson, H. Gill, K. J. Cantrell and R. J. Serne, *Environ. Sci. Technol*., 2003, **37**, 3367.
110 Y. J. Hu, L. K. Scwaiger, C. H. Booth, R. K. Kukkadapu, E. Cristiano, D. I. Kaplan and H. Nitsche, *Radiochim. Acta*, 2010, **98**, 655.
111 B. A. Powell, Z. Dai, M. Zavarin, P. Zhao and A. B. Kersting, *Environ. Sci. Technol*., 2011, **45**, 2698.
112 M. Zavarin, P. Zhao, Z. Dai and A. B. Kersting, *Radiochim. Acta*, 2014, **102**, 983.
113 A. Yu. Romanchuk, S. N. Kalmykov, A. V. Egorov, Y. V. Zubavichus, A. A. Shiryaev, O. N. Batuk, S. D. Conradson, D. A. Pankratov and I. A. Presnyakov, *Geochim. Cosmochim. Acta*, 2013, **121**, 29.


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