Century of Radiochemistry: History and Future

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Several periods in radiochemistry development history are observed. In the report the sources of radionuclide income into environment are examined including long-lived transuranic elements on the different stages of full nuclear fuel cycle. Radioactive substance contamination analysis is given for different regions of Russia from natural and man-caused sources. Potential danger of long-lived radionuclide and transuranic element presence in the wastes of nuclear fuel cycle plants is shown. Data related with the sequences of nuclear weapon testing on the proving grounds near Semipalatinsk, and Novaya Zemlya are presented. The modern radioecological situation around the reprocessing plant "Mayak", which was constructed more than 40 years ago for the production of plutonium for military purposes, is overviewed. The following topics are considered: lake Karachay; artificial water reservoirs contaminated by radionuclides; solid radioactive wastes and their vitrification. Some new approaches, methods and tools developed at the Vernadsky Institute of Russian Academy of Sciences for determination of different radionuclides in various environmental samples from the impact zone of the facility are discussed. The data on distribution, occurrence forms and migration processes of ^{90}Sr, ^{137}Cs, ^{237}Np, ^{239}Pu, and ^{241}Am in aquatic and terrestrial ecosystems are presented.

1. Introduction

A hundred years ago Henri Becquerel discovered the phenomenon of radioactivity. Seventy years are passed also from publishing of the pioneer work by George von Hevesy and Hilde Levi opened using of activation analysis. Chemistry was widely used during the long history of radioactivity study. Moreover, important regularities of this phenomenon were discovered due to application of radiochemistry.

In the history of radiochemistry it is possible to distinguish few periods.[1] The first period of radiochemistry formation as an independent scientific direction, was closely related with the discovery of new radioactive elements, understanding of the main laws of radioactive substance behavior.

During the second period (40–50-th years) the radiochemical investigations were focused on the practical utilization of nuclear energy, studying of the chemical properties of artificially obtained elements, development of technology of processing of the irradiated nuclear fuel, resolving of the problem of radioactive wastes burial.

The intensive development of activation analysis in the 50-th years was also definitely stimulated by needs in qualitatively new materials for nuclear technology (high pure carbon, beryllium, zirconium and others). Comparatively with known at that time analytical methods, only NAA due to its high sensitivity was suitable for impurities control in course of technology development.

In the 60–70-th the serious attention was paid to the analysis of different semi-conductors (silicon, germanium, gallium arsenide, tellurium, cadmium telluride and other substances), geological materials.

Later years the method begins widely to be applied for the analysis of environmental samples, for investigations in medicine and biology. Therefore, one can trace the similar tendencies in priorities like in the case of radiochemistry: the exclusive work for purposes of nuclear technology is replaced by maintenance of diverse needs of the society.

From the 60-th the society step by step began realize the global character of consequences of the contemporary activity of mankind. The main attention shifted to the problems of maintenance of the sustainable development, including such aspects as: remediation of the polluted territories, study of the radionuclides behavior in nature, reduction of the amount of unavoidable (for the current nuclear technology) radioactive wastes, development of technology of long-term radioactive wastes storage and many other things.

Today radioactive isotopes are less often used for the elements determination, but they find more and more wide application in medicine, environmental science, biology for the purposes of diagnostics, elements speciation and migration, studying of fine biochemical processes.

Environmental problems are known to be among the most important issues of humankind. Solutions to these problems in Russia are considerably aggravated by heavy nuclear pollution in many regions of the country. A number of factors have made artificial radionuclides a persistent and very dangerous environmental problem. Among these are tests of nuclear weapons in the atmosphere and underground; the activity of nuclear power plants with nuclear fuel cycles producing and accumulating weapon-grade plutonium (USA: Hanford, Savannah River, and Idaho; Russia: Mayak Production Association in Ozersk, Siberian Chemical Plant in Seversk, Mining and Chemical Plant in Krasnoyarsk- 26); the activity of nuclear power stations and, especially, the numerous accidents that occur at them; and the unsanctioned submersion of nuclear waste and the disposal of active solutions from ships and submarines with nuclear power units into various regions of the oceans. Rehabilitation of territories contaminated with radionuclides is an important environmental, economical, and social problem.

2. The Main Sources of Nuclear Pollution in Some Regions of Russia

2.1. Nuclear Tests. In the USSR, nuclear tests in the atmosphere were carried out from 1949 to 1962 in the Semipalatinsk area (124 explosions with a total capacity of 6.3 Mt releasing 0.1MCi ^{90}Sr, and 0.2MCi ^{137}Cs), and on the North Land (87 explosions, including 3 submarine ones with a total

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capacity of 250Mt releasing 4.2 and 8.0MCi of ^{90}Sr and ^{137}Cs, respectively).

In addition, Russia performed 81 commercial nuclear explosions, including those aimed at intensifying oil production, and for seismic surveying, and construction. Some of the explosions (for example, "Kristall" (l974) and "Kraton-3" (1978) in Yakutia) resulted in the emission of radioactive vapor and gas into the atmosphere, including a small amount of plutonium.

The tests of nuclear weapons have resulted in the emission into the environment of a considerable amount of uranium, plutonium, and their fission products, which were distributed as aerosols and gases across large distances and produced the anthropogenic radioactive background on the earth's surface, especially in the northern hemisphere.

The density of pollution (Bq/m^2) with the most dangerous radionuclide, plutonium, varies in different countries as follows: Germany, 67–148; Ireland, 33–l27; Great Britain, 33–122; Russia: Leningrad Nuclear Power Plant region, 14–262, Beloyarka Nuclear Power Plant region, 116–183; Mayak, up to 1400; Ukraine: Chernobyl Nuclear Power Plant (30-km zone), 3700; and Japan, 90.

2.2. Nuclear Power Plants. The commercial use of atomic energy was launched in 1954 by the installation of the first 5-MW nuclear power station in Obninsk. According to the International Atomic Energy Agency, by the time of the Chernobyl accident, 417 nuclear power units in 26 countries functioned and produced 285×10^9 W of electrical energy. According to the same agency, it is suggested that nuclear energy will continue to develop to the year 2000, and its fraction in the world's production of electrical energy will continue to grow.

By the end of 1998, 29 nuclear power units of Russia's nine nuclear power plants with an established electric capacity of 21242 MW accounted for 11.8% of total Russia's electrical energy supply. The work of a nuclear power plant is environmentally less hazardous than that of a power station that uses natural coal. Nuclear power plants release a certain amount of long-lived radionuclides (^{85}Kr, ^{3}H, ^{14}C, and ^{129}I) into the atmosphere.

Overall, the contribution of nuclear power plants to the dose of natural background radiation was less than 0.1% in the early 1980's[2] and will be less than 1% in 2000, if the expectations of its development are justified. The annual dose due to the effect of the nuclear fuel cycle (mining, processing, and extraction of uranium, production of fuel elements; work of nuclear power plants; and the reprocessing of spent nuclear fuel) is currently equivalent to the radiation that a person gains during an hour's flight in an airplane.

The main problems in the development of nuclear energy are to ensure its safety and to dispose of the high-level radioactive waste safely. In this context, potential use of the thorium fuel cycle with fluoride melts, utilization of highly enriched (up to 99.9%) ^{235}U, new technological approaches to the reprocessing of spent nuclear fuel, and transmutations of nuclear waste are now discussed.

2.3. Plutonium Production for Military Purposes and Reprocessing of Irradiated Nuclear Fuel. The production association "Mayak" (hereafter "Mayak") is located at 55°44' N and 60°54' E, 70 km north of Chelyabinsk and 15 km east of the town Kyshtym in the southern Urals and covers an area about 200 km^2 including the town Ozersk. "Mayak" was established in late 40's for production of plutonium for military purposes and for processing fissile materials to achieve a parity in the nuclear arms race. In 1945 a governmental decision was taken on selection of a construction site and the first industrial nuclear reactor was started to be built on the southern shore of the Kysyltash, while the settlement for the specialists in the field was built in a peninsula in the southern part of the Irtyash lake.[3] The first continental reactor facility, named "Annushka", was put into operation on 19 June, 1948. This day may be considered a birthday of "Mayak" and the nuclear industry of that country as a whole.

Regretfully, at the early stage of running in a number of unique and complicated technologies some serious technical mistakes were made. They aggravated ecological situation around "Mayak", harmed population and brought about intolerance among local people toward the "Mayak" activity.

The region of location of "Mayak" facilities is a unique area as regards both the scale of environmental contamination and the variety of objects subjected to the radiation impact. Significant territories around "Mayak" have undergone radioactive contamination as result of the 1957 and 1967 accidents and technological discharges into atmosphere. Discharges of liquid wastes to the river Techa at early stages of "Mayak" operation have resulted in contamination of its floodplane and radiation exposure of the local population inhabiting the shore area. At total a huge amount of radioactive wastes have been accumulated and stored at "Mayak" (about 1 billion Curies), which represent a great ecological hazard.

Nowadays, the reactor division of "Mayak" includes two operating reactors producing radionuclides both for military purpose and general applications and five uranium graphite reactors, which were shut down in 1987–1991. Production of the weapon grade plutonium at "Mayak" was stopped in 1987. The new plant operation started in 1977 and since then the staff of it has been involved in spent fuel reprocessing from different power reactors, as well as from transport and research reactors. For the whole operation period 2380 tons of spent fuel were received from a number of domestic and the foreign power plants. The plant comprises a spent fuel storage pool, three chopping-dissolution process lines, a PUREX extraction with separated plutonium, and technetium streams output. In January 1996 the waste partitioning facility was put into operation after a prolonged preparatory period. Currently the work is under way on development of the cementation and bituminization facilities for the medium level wastes utilization.

3. Current Radioecological Situation around "Mayak"

The region in which the "Mayak" facilities are located is unique with respect to both the scale of environmental contamination and the variety of objects subjected to the radiation impact. Significant territories around "Mayak" have undergone radioactive contamination as result of the 1957 and 1967 accidents and technological discharges into atmosphere. Discharges of liquid wastes to the river Techa at early stages of "Mayak" operation have resulted in contamination of its floodplain and radiation exposure of the local population inhabiting the shore area.

The river "Techa" belongs to the Iset-Tobol-Irtysh-Ob river system. In its upper reaches it passes "Mayak". Liquid waste was released 6 km from the Techa source. About 76 million m^3 of wastes which contain 2.7 million Ci of radionuclides were discharged into Techa directly.[4] About 95% of this amount (4300 Ci/day on the average) was discharged in the period from March 1950 to November 1951 and it was deposited within the first 35 km of downstream. Most part of these radionuclides were accumulated in the upper reaches of the river; however, the Iset', Tobol, and Ob' rivers, which drain successively into each other, were also contaminated. The average concentration of ^{90}Sr, ^{137}Cs and ^{239}Pu in the bottom sediments of Techa river in 1993 at the Muslimovo settlement, which is located 78 km downstream, amounted to 2.2, 0.3, and 0.025 pCi/kg respectively.

The accident of 1957 was happened due to violation of the temperature regime in the storage tank for high radioactive wastes of the plutonium production facility, which contained large amounts of sodium nitrate and acetate salts.[5] The liquid

sludge ejected to the atmosphere up to the height of 1–2 km formed a radioactive cloud which moved for 345 km to North-East from the storage site and formed a trace on the ground surface due to the aerosol precipitation. The region covered, which is named as the Ural Trace, was approximately 15000–23000 km^2 within the territories of Chelyabinsk, Sverdlovsk and Tyumen regions. The contamination of nearly 1000 km^2 exceeded 2 Ci/km^2. The percentage of the contaminated arable, haying and grazing lands within this area totalled to 40.9 and 12% respectively.

The total amount of the radionuclide substances released to the atmosphere according to different sources varies from 2 to 20 MCi ($7.4–74 \times 10^{16}$ Bq).

The major part of radionuclides has been deposited in the vicinity of the accident site. At the closest area 1 to 2 km along the trace axis 0.5–1.0 km wide the density of the soil contamination amounted to 140000 Ci/km^2, while at the area 75 km long and 7 km wide it was equal to 28 Ci/km^2.

The major part of the radioactive release consisted of the short-lived fission products (^{106}Ru, ^{144}Ce, etc.) and ^{90}Sr; their content in soils 0.5–1.0 km away from the accident site totalled to 15×10^3 and 4×10^3 Ci/km^2, respectively. Due to the decay process ^{90}Sr has gradually become the main source of the radioactive contamination of the area (99.3%). ^{137}Cs is playing a notable role. The release contained also little amounts of plutonium and uranium. The fifty years of operation of the first plutonium producing enterprise have resulted in local accumulation of large amounts of radioactive wastes (several hundred million Curies, distributed between the low-, middle- and high level liquid wastes, solid wastes in different forms).

As result of accomplishment of the military program about 19000 m^3 of highly radioactive wastes (both solutions and suspensions) with the total radioactivity of 135 MCi have been accumulated. Part of the wastes (about 8000 m^3) originated from extraction process is stored in tanks as highly radioactive nitric acid solutions with the total radioactivity of 200 MCi. In addition, every year about 2000–3000 m^3 of HLW is produced as result of nuclear fuel reprocessing from nuclear power plants and marine reactors (totalled to 100 MCi). Some data on quantity of HLW as of March 1, 1995 are shown in Table 1. The wastes accumulated are stored in the 18 special vessels with the total volume of 316 m^3 and the working volume of 285 m^3 (5 m height × 9 m diameter). Evaporated nitric acid solutions are kept in 3 tank units made from stainless steel with the working volume of 1500 m^3 each.

The wastes in form of suspensions are put into 20 storage tanks comprising concrete chambers of $19.5 \times 9.5 \times 7$ m plated by stainless steel with the working volume of 1170 m^3. Currently produced HLW originated from nuclear fuel reprocessing are subject to evaporation followed by fluxing with phosphoric acid and sodium nitrate and, finally, to vitrification in a furnace of direct electrical heating with the processing capacity up to 500 L/hr. Table 2 shows some data on amount of wastes having been vitrified over various periods at "Mayak". The molten mass is casted into special containers of a 200 L volume, which are assembled in groups of three units inside a larger container for the storage in a temporary repository. The rated specific activity of the molten mass is 2500 Ci/L, while the specific activity of the glass produced amounts to 200–600 Ci/L.

TABLE 1: Amount of High Radioactive Wastes Accumulated at "Mayak"

Type of waste	Amount, m^3	Total activity, MCi
Suspensions	19000	135
Nitric acid solutions	11700	249
Vitrified wastes	1974	246

TABLE 2: Amount of Wastes Vitrified at "Mayak"

Year	Amount, tons	Activity, MCi
1987–1990	162	3.96
1991	178	28.2
1992	563	77.7
1993	448	46.8
1994	407	57.4
1995	216	31.7
Total	1974	245.76

A wider scale HLW processing can be accomplished only after their special pretreatment involving partition technologies with application of the electric furnace installation with isolated electrodes or microwave heating unit. Currently a new partition facility for the HLW fractionation incorporating an extraction recovery of Cs and Sr by the chlorinated cobalt dicarbolide is developed. The work is under way on optimization of technological scheme of selective isolation of the long-lived alpha-emitters (uranium, neptunium, plutonium) from radioactive effluents, which is based on their extraction by the bydentate neutral organophosphorus compounds.

4. Environmental Monitoring at the "Mayak" Area

The long term radiation hazard to the contaminated territories arises primarily from the presence of long-lived radionuclides among which the actinide isotopes play a notable role. Decontamination of ground waters, basins, soils and other natural and technogenic objects from these radionuclides is the most important and very difficult problem.

In this context the knowledge of the dynamics of radionuclide migration with surface and underground waters becomes of principal importance, since it allows estimation of the efficiency of these rather expensive remediation measures. Therefore, some institutes of the Russian Academy of Sciences pursue studies on interactions between ground waters and bed rocks and on chemical and mineralogical composition of the samples taken from various sites of this zone and from various depths of boreholes. We have performed radiochemical analysis of liquid and solid samples and determined the content and the forms of occurrence of radionuclides. It should be noted that prediction of migration process is a very complex scientific problem even for such a small location owing to diversity of chemical and mineralogical compositions of environmental matrices.

Radionuclide content in rocks and waters has been determined in accordance with the procedure developed at the Vernadsky Institute.[6–10] It makes it possible to determine several radionuclides out of the same sample which saves labor time spent on sample preparation and dissolving. Analysis of soils, rocks and other solid samples includes air drying, disintegrating (milling), sieving through a 1 mm siever, igniting at a temperature of approximately 550°C to destroy the organic matter, which takes several days.[10] Radionuclides from the water samples have been concentrated by evaporation (at the Vernadsky Institute) and ultrafiltration (at the central "Mayak" plant laboratory). The last procedure enables to concentrate plutonium out of the water sample of 2 to 50 L in volume. The degree of the plutonium fixation during the water filtration through a Ripor-4 membrane (water-soluble polymers polyethyleneimin-ethylenediamintetraacetate PEI-EDTA) is practically independent of the content of the organic matter which plays an important role in colloid and complex formation. This degree amounts to 90–99% for the samples from the industrial reservoirs ^{10}B and ^{11}B, and 87–98% for the water samples from the peat bog containing 3.2, 3.3, and 29 mg of the organic carbon per liter. For the determination of radionuclides in the underground water samples collected near the Karachay Lake 10 to 100 mL of the sample is enough.

On the first stage of the applied analytical scheme prior to radiochemical analysis the gamma spectrometry using Ge(Li) detector has been performed. Determination of Sr and TUE which are pure β and α-emitters can be done only radiometrically with the radionuclide separation from a big sample of complicated chemical and radiochemical composition. This procedure needs very careful purification, especially during separation of radionuclides having almost similar energies of β and α-emission. This concerns natural radionuclides, in particular which amounts in the environments are 2 to 3 orders higher as compared with those of artificial ones. To transfer radionuclides from the ashed residue or the water concentrates it is enough to treat the samples with 7–8 M HNO, in presence of potassium bromate after their pretreatment by a mixture of HF and H_2SO_4. Further plutonium concentration and radiochemical separation has been carried out on the anionite VP-1Ap; for americium and curium the complexation sorbent polyarsenazo-n has been used; for Sr, the porous copolymer of styrol with divinylbenzole (TVEKS), impregnated with 10% dicyclohexyl-18-crown-6 (DCH18C6) in tetrachloroethane. This method is pretty selective for ^{90}Sr, but needs its careful separation from ^{210}Pb if the latter is present in comparable quantities. Therefore, the "Mayak" samples needed additional purification by preliminary elution of the radioactive ^{210}Pb by sodium oxalate solution. Radioactivity of the separated TUE has been measured at an alpha-spectrometer facility consisting of the ionization camera with a grid and an analyzer AI-4096.

Extraction and determination of neptunium is a more complicated procedure as compared with that of plutonium and americium due to the lower concentrations of the former. The method developed at the Vernadsky Institute is based on the neptunium extraction with the potassium phosphortungstate during their sorption on the porous teflon membrane impregnated with 0.5M solution of trioctylammonium nitrate (TOMAN) in toluene, which is followed by the luminescent determination. $PbMoO_4$ has been used as a crystallophosphor[9].

Detection limits of the radionuclides determination under above mentioned procedures are shown in Table 3.

TABLE 3: Detection Limits Attained for a Number of Radionuclides of Environmental Concern

Radionuclide	Detection limit, Bq/g
^{60}Co	1.2×10^{-3}
^{90}Sr	4.5×10^{-3}
^{237}Np	2.6×10^{-6}
^{239}Pu	1.3×10^{-5}
^{241}Am	2.6×10^{-5}

To predict the migration of radionuclides and to develop remediation approaches, it is necessary to determine not only the content of radionuclides in particular components of biogeocenoses, but their occurrence forms as well. As for speciation of radionuclides in solid materials, it seemed most appropriate to determine the geochemical forms of mobility.[10] These data are usually obtained by selective leaching. For loamy materials, which mostly accumulate radionuclides, the fraction of relatively mobile forms is maximum for radiostrontium, whereas for plutonium it usually does not exceed 10%. This fact explains the high concentration of ^{90}Sr in groundwater from various sites of the region as compared to plutonium and radiocesium. It is also interesting that the mobility of radiostrontium is higher than that of its natural analogues, calcium and magnesium. Our results show that the migration ability of radionuclides in the ecosystems in question increases in the following series: ^{137}Cs < $^{239, 240}$Pu < ^{241}Am < ^{90}Sr < ^{60}Co < ^{237}Np. The data on distribution of radionuclides, ^{90}Sr, ^{137}Cs, ^{237}Np, ^{239}Pu, and ^{241}Am between components of various ecosystems of Southern Ural region as well as their forms of occurrence show that ^{90}Sr, ^{237}Np, and ^{241}Am mostly involved in compounds of fulvic acids, that's why they have a high mobility in the environment. On the contrary, considerable amounts of ^{137}Cs and ^{239}Pu have been found in low soluble humid acids bonded primarily with calcium and relatively low mobile hydroxides. The data on vertical migration of plutonium, radiostrontium and radiocesium in various types of soils have been obtained and corresponding coefficients have been calculated. We consider that one of the most important factors affecting migration resistance of soil media is the content and nature of organic substances. In particular, the clear dependence between diffusion resistance of upper soil layers to plutonium and radiostrontium mass-transfer and content of humus in these layers has been determined. The correlation between migration coefficients and the content of the most mobile plutonium forms has been revealed.

5. Conclusion

It should be emphasized the most important problems of modern radiochemistry.

1. Radioactive waste management:
- The creation of brand new processes of the spent nuclear fuel reprocessing.
- The fractionation of the accumulated radioactive waste.
- The new approaches to the ensuring of long terms ecologically safe radioactive nuclides storage (repository).
- The development of new matrices and new methods of vitrification of radionuclides with different half lives.
- The development of new types of barriers (natural and man-caused) for the safe storage of the spent nuclear fuel and radioactive wastes.

2. The behavior of radioactive substance in biosphere:
- The development of principles and approaches of radiomonitoring in regions affected by nuclear plants and centers.
- The elaboration of new methods and techniques of radioecological analyses of the environment samples.
- Data gathering, systematization and computation on content and speciation of radionuclides in the environment.
- The long term forecast of the radionuclides behavior after their output into the environment.

6. References

(1) B. F. Myasoedov, Environmental Science **1**, 3 (1998).
(2) N. S. Babaev, V. F. Dermin, and L. A. Il'in et al., In *Nuclear Energy: Hurnans and the Environment* (Moscow, Atomizdat, 1984).
(3) V. I. Fetisov, Radiation Safety Problems **1**, 5 (1996).
(4) Yu. G. Mokrov, Radiation Safety Problems **3**, 19 (1996).
(5) G. N. Romanov, D. A. Spirin, and R. M. Aleksakhin, Priroda **5**, 53 (1990).
(6) B. F. Myasoedov, Journal of Alloys and Compounds **213/214**, 290 (1994).
(7) N. Yu. Kremlyakova, A. P. Novikov, S. G. Korpusov, and B. F. Myasoedov, *Patent Rus*., 4924649/25 (1991).
(8) A. P. Novikov, M. N. Mikheeva, T. I. Trofimov, and Yu. M. Kulyako, *Patent Rus*., 4897664/23 (1990).
(9) A. P. Novikov, S. A. Ivanova, M. N. Mikheeva, and B. F. Myasoedov, *Patent Rus*., 5146273/27 (1992).
(10) B. F. Myasoedov, A. P. Novikov, and F. I. Pavlotskaya, Zhurnal Analyticheskoy Khimii **51**, 124 (1996).