# ON THE MANAGEMENT OF RADIOACTIVE WASTES AND THE CONCEPT OF HAW PARTITIONING

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## ABSTRACT

The report presents information on arising of radioactive wastes in the Community countries and organizations responsible for waste storage, reprocessing and disposal.

Data are given on amounts of different wastes accumulated so far and stored in liquid and solid state, as well as in the form of vitrified blocks.

Main legislative documents regulating the waste management, as well as information on scientific organizations responsible for the development of methods for radioactive waste management are considered.

Alternative methods for management of long-lived technogeneous radionuclides, which are now under development when realizing the closed fuel cycle, are discussed including disposal into geological formations, transmutation and removal into space. Principal approaches to performing each of the methods mentioned-above are reviewed.

Concept of HAW partitioning with recovery of TUE and long-lived fission products into individual fractions is described. A review of developments is presented concerning the extraction methods with carboranes, crown ethers and bidentate extractants, as well as the sorption methods with the use of ferrocyanide materials and ampholytes.

## ORGANIZATION OF ACTIVITIES ON WASTE MANAGEMENT IN THE SYSTEM OF MINISTRY OF NUCLEAR POWER AND INDUSTRY

Safe and ecologically reliable isolation of radioactive wastes from biosphere poses a special problem, the solution of which is responsible in the final analysis for rates and scales of nuclear power development in the Community countries and in the world as a whole.

In our country there are the following arisings of radioactive wastes:

- at nuclear power plants, radiochemical plants and other installations of nuclear fuel cycle (NFC);
- on performing the military programs and on operating the nuclear power ship installations;
- on conducting different research programs;
- in industrial and agricultural enterprises, in medical and educational institutions when using the sources of ionizing radiation and isotopes;
- on purification of contaminated territories of nuclear objects.

Responsibility for radioactive waste management in civil sectors of medical institutions, agriculture, research reactors a. o. rests primarily on the governing bodies of these organizations. For storage and disposal of the wastes, there have constructed regional burial sites, including 16 sites in Russia and 5 - Ukraine.

Within the frames of defense programs, at radiochemical plants of the Ministry about $1 \cdot 2 \cdot 10^9$ Curies of liquid radioactive wastes are accumulated and stored in special containers, $1 \cdot 10^6$ Curies of solid wastes are stored in nearsurface facilities. Accident situations, without consideration of the Chernobyl accident, have led to contamination of territories over a total area of 90 thousand hectares, about 60 thousand hectares are occupied by dumps and remainders from mining enterprises.

Late in 1991, more than 310 tons containing about $3 \cdot 10^7$ Ci were stored in vitrified state. At nuclear power plants, liquid radioactive wastes of low activity (135000 $m^3$), solidified waste (8000 $m^3$) of 800 Ci activity and 100000 $m^3$ of solid wastes contaminated by radioactive substances (equipment, debris a. o.) are stored.

Research institutes, construction organizations and industrial enterprises in Russia carry out the main elaborations of methods for radioactive waste management, conduct fundamental and applied investigations in this area and design the necessary equipment.

Management of radioactive wastes is regulated in our country by "Basic sanitary rules", "Code of radiation protection" and "Regulations for transporting the radioactive substances".

All-Union Research Institute of Inorganic Materials was appointed as headquarters organization in the field of waste management problem; this institute accomplishes the scientific guidance concerning the reprocessing and interim storage of radioactive wastes arising in the industry. Designing the facilities for waste management, execution of technical-economic calculations and scientific guidance in transportation of radioactive materials - all these activities were entrusted to the All-Union Research and Design Institute of Power Technology (St. Petersburg). All-Union Research and Design Institute of Industrial Technology (Moscow) performs designing and scientific research work connected with construction of underground burial sites for radioactive wastes.

Scientific-production Association "V. G. Khlopin Radium Institute" (St. Petersburg) develops methods for HAW

management in the system of nuclear fuel reprocessing, conducts combined investigation of environmental impact of NFC installations and carries out also radioecological monitoring.

Considerable scope of research and development is performed at All-Union Research Institute of Nuclear Power Plants (Moscow), at Research Institute of Chemical Machinery (Ekaterinburg), at Research Institute of Chemical Technology (Moscow) and directly at industrial enterprises as well.

The first deputy minister, professor B. V. Nikipelov is a leader of work on problems of radioactive waste management. Three central administrative boards are responsible for direct performance of research and development, among them the Head scientific-technical board accomplishes the coordination of works and financing of main directions in research and development.

The branch program for radioactive waste management developed in 1989-90 is focussed on comprehensive solution of radioactive waste problem at operating, designed and under construction plants, from standardization of waste processing procedures to safe isolation from biosphere. Now a database is created on quantities, characteristics and arisings of wastes at installations of the Ministry. Expenditures for research and development work in the nearest years are estimated in 80-100 mln. roubles per year (prices of 1991).

Of great importance remains the problem of developing a package of legal, administrative and economic measures aimed at revealing all sources and reducing the amounts and volumes of radioactive wastes at NFC installations. A law of nuclear power including an issue of radioactive waste management is now under preparation.

At NPPs, mining and processing enterprises of NFC, construction of installation complex is envisaged for reprocessing and storage of all categories of wastes, local and regional waste storage facilities, recovery work for contaminated areas.

For low- and intermediate active wastes, the near-surface burial sites providing safe isolation with monitoring system, the installations for incineration, compaction, cementation and bitumization are designed. Different technologies for processing of gas effluents are realized.

## ON HAW PARTITIONING AS APPLIED TO SUBSEQUENT ALTERNATIVE TECHNIQUES FOR MANAGEMENT OF LONG-LIVED RADIONUCLIDES

### Geological Disposal

Long-lived radionuclides present most difficulties in solving the problem of radioactive waste management. While for nuclides with life period no more than 1000 years some acceptable means existing for isolation from biosphere, as far as the nuclides with activity retaining for tenths, thousands, hundreds years and more is concerned, several containment concepts are now under consideration, the most essential of which is disposal into deep geological formations.

According to this concept, physico-chemical form of waste and rocks of geological formation are considered as the main barriers. Waste packaging and isolating engineered facilities could be used as additional barriers for a limited time. Hazardous effect of wastes should not spread over the boundaries of rock site for the whole burial time. Geological formations should provide isolation of HAW and wastes containing long-lived nuclides, even under extreme situations - natural calamities and military operations.

Different versions for fabricating the stable matrices as physico-chemical form of wastes for subsequent disposal are now under development in our country. This concerns primarily the vitreous materials which are commercially produced at the Association "Mayak" (one-stage process). It is believed that the matrix of borosilicate glass is suited to disposal of radioactive wastes with life time up to 1000 years.

For underground disposal of nuclides with life time over 1000 years, mineral-like compositions could be used. So, different modified materials of Synroc type which was first proposed by a group of Australian specialists headed by Ringwood, as well as compounds of other classes (minerals of zircon group, granate, cubic zirconium a. o.) are studied. The essentials of widening the nomenclature of minerals promising for inclusion of long-lived nuclides are primarily based on those advances which have been made for the last decade in the area of HAW partition, development of new processes and equipment for denitration (plasmachemical denitration) and elaboration of new methods for high-temperature synthesis of minerals (induction melting in cold pot, isostatic pressing).

Possibility for recovery of long-lived nuclides into individual fractions which do not contain any stable salts offers the ways for solution of the problem concerning the non-conformity of radioactive waste components with the structure of mineral-like base by using differential crystalline matrices; the last achievements in elaborating the methods of high-temperature synthesis enable to design efficient hermetic remote small-sized equipment wherein the synthesis processes could be conducted at temperatures up to 2000°C and pressures up to 1500 atm.

It should be ultimately emphasized that the concept of safe containment of long-lived nuclides is to be regarded actually as having no alternatives, as in any partitioning process, in solution after separation of nuclides, along with ballast salts, some amount of particularly hazardous radioelements is always present and should be ecologically safety buried only in the earth conditions. Therefore, in our country the investigations are started with the aim of solving the top-priority tasks as follows:

- development of database for establishing the standards of permissible releases of long-lived and alpha-nuclides buried in geological formations to the human environment;
- elaboration of requirements on rock massif, artificial barriers and matrices;
- prospects in nomenclature of long-lived radionuclides and amounts to be safely buried in a limited site of rock massif;
- development of processes for partition recovery of long-lived nuclides from solutions with efficiency satisfying the conditions for further containment of solidified wastes in geological formations;
- ecological technical and economic studies of possibility and feasibility in designing the optimum system for final isolation of long-lived nuclides from the sphere of human activity, which envisages methods

of transmutation and space isolation in addition to the method of underground burial.

**Transmutation of Long-Lived Radionuclides**

Careful separation into individual fractions is also required in the case of transmutation method, i. e. nuclear transformations of long-lived radionuclides into short-lived or stable ones.

Early in the eighties, the IAEA drew essentially negative conclusions concerning the expediency of developing this program. Late in the eighties, interest for nuclear transmutation of long-lived radionuclides was shown again. This results in the development of "OMEGA" program (Japan) and other national programs.

At the IAEA consultative meeting in October 1991, the representatives from 13 countries support the developments in the area of partition - transmutation of long-lived radionuclides. Attractiveness of the transmutation concept for its followers is caused by different reasons. Some consider this alternative as a mean for persuasion of public opinion in acceptability of nuclear power, others-as a basis for improvement of radioactive waste management, the thirds have difficulties with the choice of final disposal sites, the fourths regard it as a basis for passing development of new technologies.

In our country which adheres to the position of closing fuel cycle, the R & D in partition transmutation are considered as integrated part of long-term program on radioactive waste management. The development program of partition-transmutation includes all the most important aspects, from radioecological substantiation of enumeration of radionuclides, calculation of radiotoxicity indices, substantiation of necessary recovery, elaboration of transmutation techniques to economic calculations of the program costs which should incorporate not only expenses for the program realization, but also take into account prevented damage to the next humanity generations. (2)

Among the most hazardous long-lived nuclides which make the main contribution to the impact on the biosphere (isotopes of plutonium, curium, americium, neptunium-237, iodine-129, carbon-14, technetium-99, cesium-135, zirconium-93), plutonium, americium and curium isotopes should be considered as real candidates for transmutation in existing types of fast reactors.

**Removal of Long-Lived Radionuclides Into Space**

Basically, for final isolation of the most hazardous wastes from the earth's biosphere, outer space could also be used. Long-term astrophysical forecast of waste fate is more reliable than the similar forecast for geological formations which vary with time.

Space isolation could be proposed for such long-lived radionuclides as technetium-90, neptunium-237, iodine-129, zirconium-93. Moderate gamma-activity and rather small volume of these nuclides make it possible to use the available technical systems for removal into outer space.

Among the variants of space isolation of radioactive wastes, both delivery of containers to the orbits in the near Sun space removal from the Sun system by using the available carrier rockets of the type "Zenith" and "Energy" are discussed.

Analysis of real reliability of rocket-space systems with due regard for many years' operating experience has shown that the required safety could be in principle achieved on multilevel countering the abnormal situations.

In connection with the specificity of this method, besides the substantiation of its economic reasonability and solution of all technical problems, the fate of the method will depend on sufficient demonstration of its reliability. Wide public opinion seems to be formed under conditions of a priori denial of such a way. This is confirmed by a rather restrained reaction of participants at the International forums where we had reported about our program.

We understand that the realization of this program requires many R & D in existing and new radiochemical technologies for separation of the most hazardous radionuclides in concentrated form with following capsulation. The wastes placed in special containers should pass standard load tests on transporting, as well as accident effects when entering into the dense atmospheric layers, impact on rock ground, exploding of carrier-rocket and fire on start.

Containers with waste simulators (without any radioactive materials) are now prepared to testing under accident conditions.

In our opinion, the program of waste removal into space could be carried out only in the frames of frank and agreed international cooperation, which would enable to choose the most safe site for starting complex and to gain all advantages from technical and economic collaboration between interested countries, including the international examination of projects.

On summarizing the foregoing about the concepts of long-lived technogeneous radionuclides, it should be noted that these concepts are not opposed. According to our position reasonable combination of the methods based on different concepts seems to be optimum solution of the problem.

## DEVELOPMENT OF METHODS FOR PARTITIONING ACTINIDES AND INDIVIDUAL FISSION PRODUCTS FROM HAW

A short review of alternatives in management of long-lived technogeneous radionuclides has shown that each of them involves a preliminary partitioning stage. Below, some existing methods and those now under development intended for HAW separation and purification of the most important nuclides for further use are discussed.

**Separation of Neptunium, Zirconium, Technetium, Iodine and Carbon-14 Within a Modified Purex-Process**

The modified Purex-process provides recovery of neptunium, zirconium, technetium, iodine and carbon-14 in the course of spent fuel dissolution and an extraction cycle for uranium and plutonium separation. In this case, neptunium is removed within the limits of the first cycle as an independent product.

The problem of purification from iodine resolves itself to localizing the zone for iodine distillation from aqueous phase into gas one on fuel dissolution, to minimizing the amount of iodine in solution and further decontaminating the gas-air flow.

As iodine in off-gases may occur in the form of molecular iodine, iodides, organic iodides, inorganic iodide aerosols a. o., it is necessary to use combined systems of liquid absorbents. Combination of such methods affords off-gas decontamination degree up to $10^2$.

Flowsheet is based on simultaneous removal of iodine and iodine oxides from gas flow, iodine blowing-off from regenerated nitric acid by capturing with alkaline solutions and separation of iodine from alkaline in the form of low soluble iodide.

Recent progress in studying the chemistry of technetium of spent fuel reprocessing has confirmed the possibility of regulating the behavior of technetium in the flowsheet. One of such methods relies on quantitative recovery of technetium into extract of uranium and plutonium and removal of technetium along with neptunium. After sorption processing of this product with subsequent crystallization of potassium pertechnetate, irretrievable losses of technetium do not exceed 0.5%.

A method for separation of technetium within the TBP extraction process on spent fuel reprocessing has been proposed. By adjusting the acidity in extraction cascade for recovery of uranium and plutonium, more than 95% of zirconium from feed spent fuel solution could be separated into plutonium reextract.

**Recovery of Cesium, Strontium, Rare Earths and Transplutonium Elements**

Proceeding from the scope of nuclides to be separated and purified, the selective recovery of TPE, RE, cesium and strontium is the most complicated task of HAW partitioning. In the world practice different techniques for recovery of above-mentioned HAW components have been tested to one or another scale, including precipitation, sorption, extraction, chromatography.

Combination of these methods makes it possible to suggest several complex flowsheets for HAW partitioning which enable to obtain fractions of long-lived radionuclides for further transmutation. One of such promising partition flowsheets is elaborated jointly by V. G. Khlopin Radium Institute and Institute of Nuclear Research (Czechoslovakia). (4, 5)

This flowsheet is based on using as extractant chlorinated cobalt dicarbolyde in polar diluent which permits to recover cesium, strontium, TPE and RE into individual fractions. The process proceeds without any adjustment of acidity in initial liquid HAW and is versatile as applied to different types of radiochemical wastes.

In the course of pilot testing of the flowsheet at the production association "Mayak", the proposed technology has furnished the fractions of cesium, strontium, TPE and RE with recovery degree over 99%. Further efforts by the authors of this HAW partition method are directed towards more complete recovery of components, handling of secondary wastes, improvement of the flowsheet, automation of process control.

Extraction recovery of strontium and cesium is also studied by the use Crown ethers (dicyclohexl-18-Crown-6 for strontium and dibenzo-21-Crown-7 for cesium). Sorption method for cesium recovery with ferrocyanide-containing inorganic sorbents was tested on real solutions on a commercial scale.

For TPE recovery, the use of bifunctional neutral phosphororganic compounds (in particular, the solution of diphenyl dibutylcarbamoylmethyl phosphine oxide and solid extractants on their basis is investigated as well. With the aim of fabrication of microspheres from TPE titanates and zirconates, a process for separation of TPE from liquid HAW by ampholities is studied.

The detailed data on development in HAW partition are given in reports presented by the Soviet specialists in the Section N 22 of this Symposium.

## CONCLUSION

A program for waste management which is developed by Soviet scientists is focussed on combined solution of the problem for operating, planned and constructed objects, from standardization to safe isolation from biosphere. Database is created on quantities, characteristics and arisings of wastes, as well as storage and disposal sites.

Basic concept for management of long-lived radionuclides envisages the inclusions of them into strong matrices and the disposal into deep geological formation after the choice of burial sites.

For realization of above concept, a scientific-research program has been developed; it includes the following:

- the establishment of standardized values for permissible releases of TPE and long-lived nuclides in the environment on the basis of a unified criterion, reasonable risk of individual and collective exposure doses and working-out the appropriate requirements on the combined system: rock massif, matrix with incorporated radionuclides;
- predicated estimate of nomenclature of long-lived radionuclides and amounts which could be safely (in accordance with radioecological requirements) disposed of in a limited volume of rock massif and working-out the requirements on recovery degree for TUE and long-lived fission products;
- ecologo-technical and economic evaluations for expediency to supplement the method of underground disposal by the methods of transmutation and space isolation.

For some hazardous nuclides and, first of all, transuranium elements, the alternative option of nuclear transmutation is studied, including the following aspects:

- substantiation for enumeration of nuclides to be subject to transmutation;
- calculation of radiotoxicity indices for radionuclides and substantiation of necessary degree for their recovery;
- elaboration of technical means for transmutation;
- economic calculations for evaluating the program costs with allowance for the prevented damage in the future.

For such radionuclides as technetium-99, neptunium-237, iodine-129, zirconium-93, potentialities are studied for space removal with the exception of any effect of these wastes on near-earth space even in the distant future. The given program could be executed only within the framework of international cooperation and should comprise the investigation of safety aspects at all stages of space launching. Now the preparation is conducted to the tests of ampoule containing radioactive waste simulator under accident conditions.

The above concepts are not opposed. It is possible that the management of long-lived radionuclides will call for reasonable combination of different options.

Each of the alternatives under development implies preliminary partition of HAW which furnishes pure individual components or radionuclide groups. In our country some developments of HAW partitioning tested in industrial or pilot scale have been accomplished. The combined extraction flowsheet for recovery of cesium, strontium, TPE and RE fractions with ChCoDiC has successfully undergone tests in commercial scale.

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