Journal of NUCLEAR SCIENCE and TECHNOLOGY, Supplement 3, p. 548–551 (November 2002)

Methods of High-Sensitive Analysis of Actinides in Liquid Radioactive Waste

Alexandre A. DIAKOV*, Tatiana N. PEREKHOZHEVA, Elena I. ZLOKAZOVA

Sverdlovsk Branch of Research and Development Institute of Power Engineering, Zarechny, Sverdlovsk region, 624250, Russia

A complex of methods has been developed to determine actinides in liquid radioactive waste for solving the problems of radiation, nuclear and ecological safety of nuclear reactors. The main method is based on the radiochemical separation of U, Np-Pu, Am-Cm on ion-exchange and extraction columns. An identification of radionuclides and determination of their content are performed using alpha-spectrometry. The microconcentrations of the sum of the main fissile materials U-235 and Pu-239 are determined with the usage of plastic track detectors. An independent method of U-238 content determination is the neutron activation analysis. Am-241 content is possible to determine with gamma-spectrometry.

KEYWORDS: actinides, liquid radioactive waste, radiochemical process, alpha-spectrometry, plastic track detectors

1. Introduction

The Sverdlovsk Branch of RDIPE has the operating nuclear research reactor IVV-2M. It neighbours by the Beloyarskaya NPP, where two Units have reached their decommissioning phase. In order to assess radiation and nuclear safety of operating and shut down reactors and develop a safe decommissioning technology, the specialists need to know the isotopic composition of actinides present in liquid radioactive waste (LRW) and nuclear reactor coolants.

The set of methods to solve the task is as follows:

- the radiochemical method including alpha-spectrometry at the final stage to indicate most of the actinides in LRW;
- the plastic track detector method to determine microconcentrations of the main fissile materials ^{235}U and ^{239}Pu as a total;
- the neutron activation analysis and gamma-spectrometry methods to detect ^{238}U and ^{241}Am.

II. Radiochemical Method

When plutonium and uranium are determined in highly mineralised solutions of LRW, Pu is deposited on the anion specific resin VP-1AP and U is precipitated on the copolymer of styrene with divinylbenzene impregnated with trioctyl phosphine oxide (TOPO). After removing impurities and eluation of actinides the sources for alpha-spectrometry are made by a coprecipitation of U and Pu with cerium hydroxide or electrical precipitation[1].

An analysis of the bottom sediments in the tanks with LRW is a more complicated task. The actinides, present there, can be of various forms. The variety can include some fine-dispersed particles of the fuel and amorphous forms of the actinide compounds in both of the conditions: free and incorporated into the matrix of oxides of macrocomponents. Hence, it becomes more difficult to determine the concentration of actinides in the bottom sediments because they have to be dissolved and separated from iron and other corrosion products.

The issues of the dissolution of fine particles of nuclear fuel were studied in details[2] after the Chernobyl accident. It was proved that nitric acid leaching could be insufficient in that case. Samples need a treatment by mineral acids in the presence of hydrofluoric, chloric acids and oxidizers. The fluorine-nitric leaching is more preferential for its high efficiency and simplicity of a removal of fluorine ions from a development solution by boiling down.

Iron and other elements of corrosion origin should be separated to the uppermost extent. The impact of these elements reveals itself at the stage of the preparation of an alpha-spectrometric source. Iron is known for its high capability to hydrolysis and it penetrates to a source during electrical deposition or coprecipitation, which deteriorates the quality of alpha-spectrum. It was shown experimentally that iron could be fully extracted by washing VP-1AP or TOPO with the increased amount (7.5 M) of HNO_3 to attain the negative reaction to iron ions at the "purification" stage. The scheme of the determination of uranium and plutonium concentration in LRW and bottom sediments is given in **Fig. 1**.

At the NPP units under decommissioning, LRW is characterised by the presence of younger actinide radionuclides (U, Pu, Np, Am, Cm) with alpha radiation from ^{241}Am prevailing due to the old age (~ 20 years) of LRW. The radionuclides of ^{237}Np, ^{241}Am, ^{242}Cm, ^{244}Cm are not less biologically important than plutonium radionuclides as the former are more mobile in ecological systems, including a human being, and accumulated by the systems as a result of a decay of other actinides. Therefore the determination of americium, curium and neptunium concentration in the LRW and bottom sediments

* Corresponding author, Tel. +(343-77)362-64,
Fax. +(343-77) 333-96,
E-mail: dyakov@sfti.zar.ru

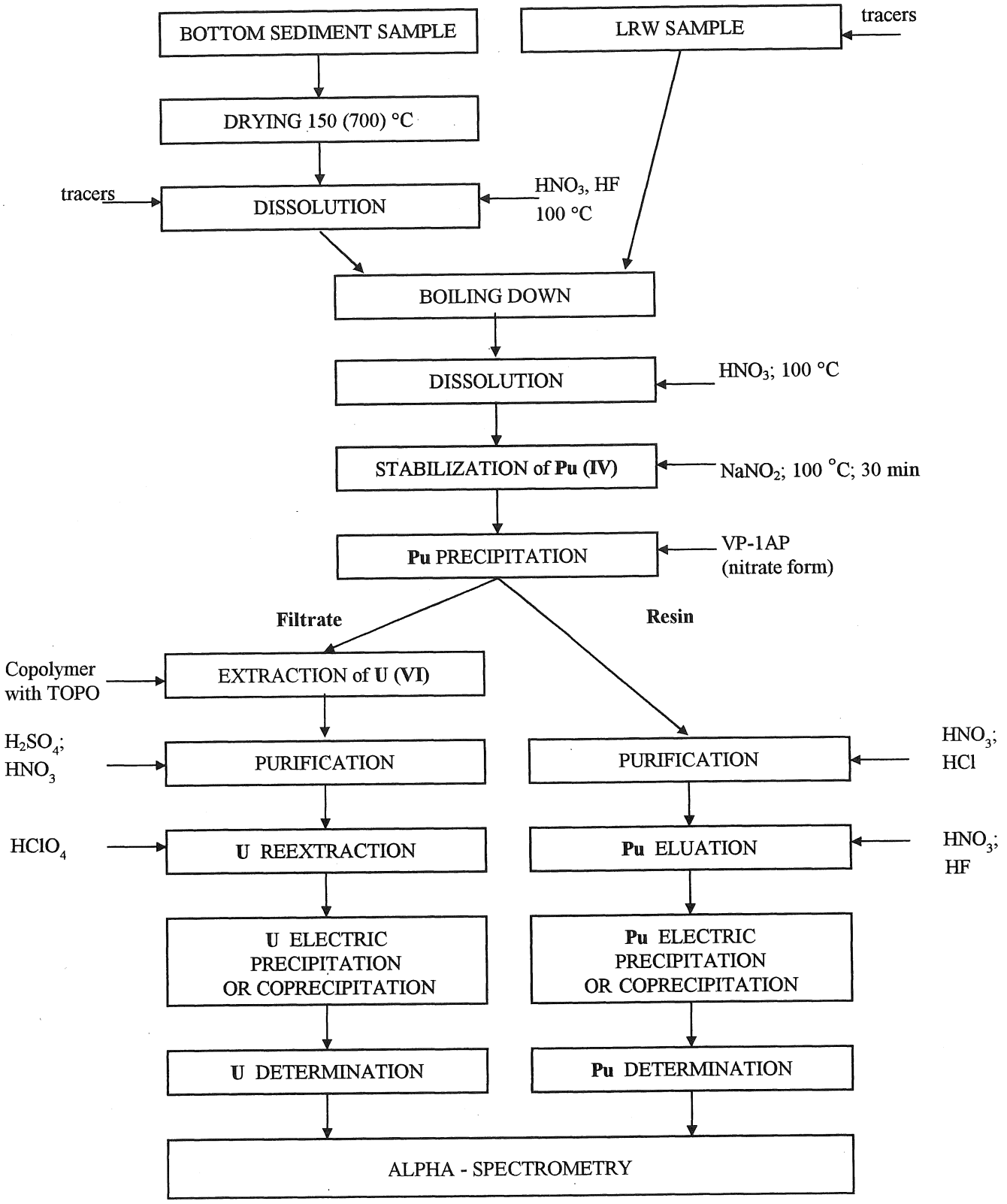

Fig. 1 The determination of uranium and plutonium concentrations in LRW and bottom sediments (scheme of procedure)

in spent fuel storage pools and LRW tanks is an urgent problem. The above mentioned method allows to determine only U and Pu.

The process of actinide separation is known, it was developed by L.I. Gouseva et al.[3] in the V.I. Vernadskii Geo-chemical Institute. The method is based on the

separation of Am and Cm from water-alcohol media on the resin Dowex-1 (the Russian analog is AB-17). This procedure was improved and added to obtain a new method of separate extraction of the fractions of U, Pu (Np) and Am (Cm) and purification of impurities like iron and the radionuclides ^{90}Sr and ^{137}Cs. A radiochemical yield was (0.5±0.1) for U, (0.8±0.1) for Pu and (1.00±0.05) for Am and Cm. The procedure is simple, reasonable and does not require expensive equipment and reagents.

The electrical deposition was performed in electrolyte cells. A Pt wire spring as anode was placed inside a quartz cylinder. Polished stainless steel disks were used as cathode. The yield of Pu was 97±3%, that of Am was 82±8% and that of U was 88±4%. A reproducibility of the method is satisfactory. The thin films of the precipitates on the disks demonstrated a typical metal colour and tight adhesion to the metal substrate.

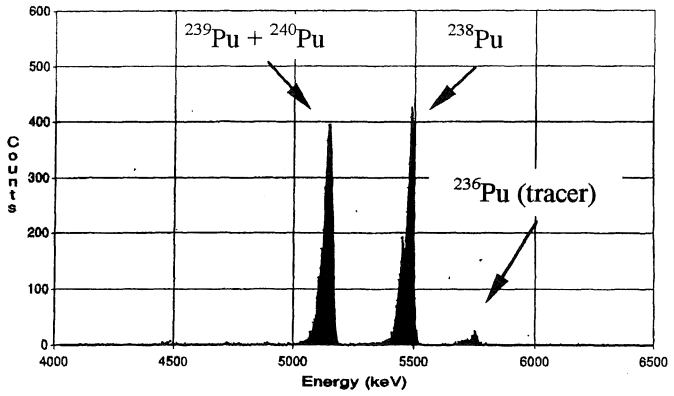

Fig. 2 Alpha-spectrum of plutonium fraction of the sample of bottom sediments in the tanks with LRW

The developed procedure of radiochemical analysis is oriented on the alpha-spectrometric determination of actinides. The method provides a reliable identification of nuclides and determination of their activities with a low detection limit. **Figure 2** shows an example of alpha-spectrum of plutonium fraction of the sample of bottom sediments in the tanks with LRW.

The alpha-spectrometer is built on the equipment and soft wear of the company Canberra Industries, Inc., USA. Its main components are the silicon detector of the type A300-17 AM with the energy resolution 17 keV on the line 5486 keV of the nuclide ^{241}Am, the control card of the multichannel analyser AccuSpec A (on-board Wilkinson ADC and 32 kB memory) and the soft wear Genie-PC.

The radiochemical process, electrolytical precipitation and alpha-spectrometry provide the energy resolution 17-25 keV and reliable identification of the following nuclides : U-232, 233, 234, 235, 236, 238; Np-237; Pu-236, 238, 239+240, 242; Am-241, 243; Cm -242, 243, 244. The range of the measurement of specific activity in the sample is from 0.8 Bq/kg to 16 kBq/kg. The alpha-spectrometer and the measurement procedure were qualified by the D.I. Mendeleev Center VNIINM, Saint-Petersburg, Russia.

III. Method of Plastic Track Detectors

An assessment of nuclear safety is based on the determination of the concentration of the fissile materials ^{235}U and ^{239}Pu. However, a small concentration of ^{235}U and its low specific activity make impossible the alpha-spectrometric determination of ^{235}U in the bottom sediments and water. The task was solved for ^{235}U with the usage of the plastic track detectors (PTD), i.e. by a "wet" variant of the method[1]. It means that the detector is exposed to neutron irradiation in the investigated solution for some period. The fission fragments of ^{235}U (or other fissile material) make tracks on the surface of the detector, their density is linearly related to the concentration of ^{235}U in the solution. The plastic track detector material is polyethyleneterephtalate.

The method of analysis is as follows. A polyethylene capsule of 30 cm^3 volume is filled with the solution investigated and 2 detectors of the size (30×40) mm are placed there. A case containing 4 such capsules is irradiated by thermal neutrons to a fluence of $2 \cdot 10^{14}$ cm^{-2} to $1 \cdot 10^{16}$ cm^{-2} in the channel of the reactor IVV-2M, where the ratio of thermal to fast neutron density is 200:1 ($E_{f.n.}$ >1.15 MeV). A neutron fluence distribution over a height of the case is controlled with activation indicators made of scandium. In each case there is a capsule with the uranium solution of the known concentration. After irradiation all the 8 detectors of 4 capsules are etched electrochemically at a time[4]. At the optimised etching parameters the contrast discharge spots of the diameter (100-150) μm are observed on the detectors, the density of the spots are evaluated for the area of 3 cm^2. **Figure 3** shows an example of PTD.

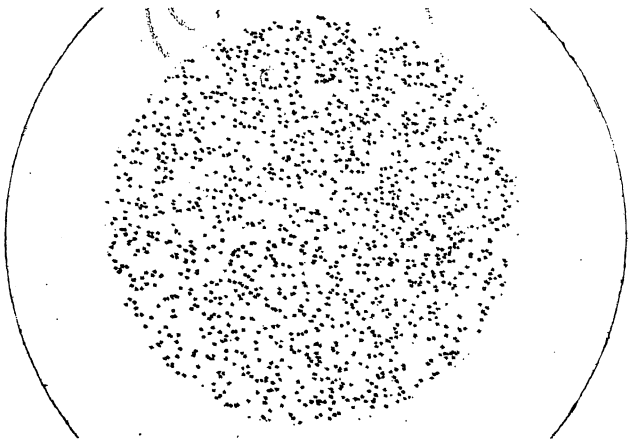

Fig. 3 General view of PTD etched electrocemically

A working range of the densities of the discharge spots is from 50 to 2000 cm^{-2}. Any unknown concentration of fissile

material is determined by the relative method. It compares the density of discharged spots on a detector in the solution investigated with that in the reference solution. The data on ^{46}Sc obtained by gamma-spectrometry are used to control the nonuniformity of neutron fluence over the height of the case.

The discharge spots on the detectors, irradiated in the solutions of the bottom sediments of the spent fuel storage pools, were formed by the contributions of both ^{235}U and ^{239}Pu. The contribution of the rest actinides was negligibly small. Since the concentration of ^{239}Pu was determined quite reliably by alpha-spectrometry, then the concentration of ^{235}U in the development solutions was obtained by the subtraction of the value of the ^{239}Pu concentration from that of the total of fissile materials, $^{235}U+^{239}Pu$, with the account of the difference in the fission cross-sections of thermal neutrons, 582 barn for ^{235}U and 742 barn for ^{239}Pu[5].

Thus, the combination of the radiochemical and PTD methods allows to estimate in full a radiation and nuclear safety of LRW storage pools and other facilities of a NPP.

IV. Neutron Activation Analysis and Gamma-Spectrometry Methods

An independent method of determining ^{238}U is the neutron activation analysis (NAA). NAA as well as PTD method helps to avoid using the complicated procedure of radiochemical precipitation of actinides.

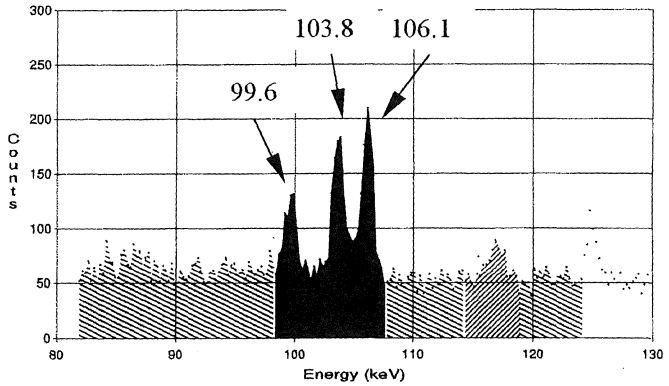

Fig. 4 Gamma-spectrum of the nuclide ^{239}Np

As for the bottom sediments in the tanks with LRW, the proven NAA procedure is as follows. The 50 mg sample of bottom sediment was irradiated by thermal neutrons of the flux density $1.5 \cdot 10^{12}$ $cm^{-2} \cdot s^{-1}$ during 6 hours in the channel of the IVV-2M reactor. For the decay period of 5 days the samples were measured with gamma-spectrometer, when gamma-quanta of the energies 103.8 and 106.1 keV of the nuclide ^{239}Np ($T^{1/2}$ = 2.36 days) were being registered. **Figure 4** shows an example of gamma-spectrum of the nuclide ^{239}Np.

An energy resolution of the germanium detector in this range was 1.0 keV (the detector type GC 1019, Canberra Industries, Inc., USA). The detection limit for ^{238}U in the sediment was ($1 \cdot 10^{-6}$-$1 \cdot 10^{-4}$) g/g and it was dominated by the Compton scattering of gamma-quanta with the energies 1369 keV and 2754 keV of the nuclide ^{24}Na ($T^{1/2}$ = 15.0 hr).

In several cases the nuclide ^{241}Am ($T^{1/2}$ = 432 yrs, E_γ = 59.53 keV) in the samples of LRW and sediments was determined by the high resolution gamma-spectrometry. The NAA and gamma-spectrometry are the means of independent control of the quality of U and Am fraction extraction from the initial probe to the final alpha-spectrometric source by the radiochemical method.

VI. Conclusion

The set of the methods to determine the actinides in LRW of NPPs is developed. The set is based on the radiochemical method with alpha-spectrometric procedure at the final stage and complimented by the PTD, NAA and gamma-spectrometry methods. Such approach allows a reliable solution of the problems of radiation, nuclear and ecological safety of nuclear reactors. These methods are rather universal and applicable for environmental monitoring.

References

1) A.A. Diakov, V.Yu. Rostovtsev, T.N. Perekhozheva, E.I. Zlokazova, "Using plastic track detectors to solve radiation safety problems at nuclear reactor facilities, " *Radiat. Meas.*, **28** [1-6], 357 (1997).

2) F.I. Pavlotskaya, "The main principles of radiochemical analysis of natural environment objects and methods to determine the radionuclides of strontium and transuranium elements, " *J. Analyt. Chem*, **52** [2], 126 (1997), [in Russian].

3) L.I. Gouseva, I.A. Lebedev, B.F. Myasoedov, G.S. Tikhomirova, "An extraction of transplutonium elements on ionites in water and alchohol media, " *Radiochemistry*, **17** [2], 321 (1975), [in Russian].

4) A.A. Diakov, L.I. Menkin, S.G. Karpechko, "A determination of uranium concentration in water coolant of the first circuit of nuclear reactor," *Atomnaya Energia*, **61** [5], 334 (1986), [in Russian].

5) B.M. Kolobashkin, P.M. Rubtsov, "Radiation characteristics of irradiated nuclear fuel," *Reference book*, Energoatomizdat, Moscow, 384 pages (1983), [in Russian].