Determination of uranium concentration and burn-up of irradiated reactor fuel in contaminated areas in Belarus using uranium isotopic ratios in soil samples

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Summary. An analytical method is described for the estimation of uranium concentrations, of $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios and burn-up of irradiated reactor uranium in contaminated soil samples by inductively coupled plasma mass spectrometry. Experimental results obtained at 12 sampling sites situated on northern and western radioactive fallout tails 4 to 53 km distant from Chernobyl nuclear power plant (NPP) are presented. Concentrations of irradiated uranium in the upper 0–10 cm soil layers at the investigated sampling sites varied from 2.1×10^{-9} g/g to 2.0×10^{-6} g/g depending mainly on the distance from Chernobyl NPP. A slight variation of the degree of burn-up of spent reactor uranium was revealed by analyzing $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios and the average value amounted to 9.4 ± 0.3 MWd/(kg U).

Introduction

As a very important parameter of irradiated reactor fuel, the burn-up allows the estimation of the quantities and the ratios of the isotopes produced in a nuclear reactor. In radioecological practice after the accident at the Chernobyl nuclear power plant (NPP), the average burn-up value calculated for the reactor core was often used for an estimation of the amounts of different actinide isotopes in the nuclear fallout by applying corresponding correlation ratios for different isotopes. In particular, this approach was used for the retrospective estimations of irradiation doses created by short-lived radionuclides, if corresponding monitoring had been not performed at the proper time.

According to calculations by Begichev *et al.* [1], the average burn-up of the 4th Chernobyl reactor was about 11.4 MWd/(kg U) when the reactor was destroyed. However, the real burn-up varied significantly over the reactor core, because spent fuel had been gradually replaced by freshly enriched uranium and the fuel assemblies had different core histories. Fig. 1 demonstrates the distribution of the burn-up of reactor uranium in the 4th Chernobyl reactor [1]. During the accident, the fuel assemblies were for the most part destroyed and a partial homogenization of irradiated uranium occurred. This especially concerned the fine particulate fuel fraction which was distributed over large distances from the reactor. However, because of the heterogeneity of nuclear fuel burn-up in the reactor core and in view of the fact that only a relatively small amount of the irradiated nuclear fuel (according to the most plausible estimations it was about 3%) entered the atmosphere, the real burn-up and the isotopic composition of actinides and fission products could vary in different contaminated areas. In addition, the accidental release of irradiated fuel continued for several days whereas the wind directions, and hence radionuclide spread, changed during different stages of the reactor accident.

Different approaches can be applied for evaluating the burn-up of Chernobyl reactor fuel by using, for instance, isotope ratios of fission products (caesium, neodymium *etc.*) or actinide (uranium, plutonium) isotope ratios [2]. The determination of uranium isotope ratios allows a direct evaluation of the degree of utilization of enriched reactor fuel, and as such represents the easiest way to calculate the burn-up. However, in contaminated soil samples, reac-

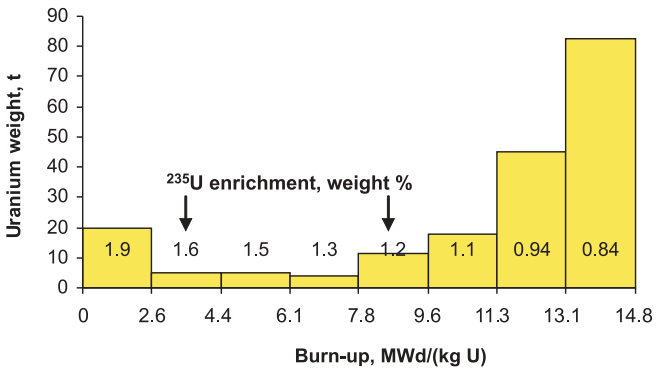

Fig. 1. Burn-up distribution and ^{235}U enrichment in fuel fractions of the damaged Chernobyl reactor, calculated data by Begichev *et al.* [1].

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tor uranium is mixed with natural uranium and therefore the $^{235}U/^{238}U$ isotope ratio deviates significantly. On the other hand, ^{236}U ($T_{1/2} = 2.3416 \times 10^7$ years) was found with very low abundance in natural uranium (the $^{236}U/^{238}U$ ratios measured recently in natural uranium ores [3–6] ranged from 1.2×10^{-11} to 5.6×10^{-10}), but it is produced in nuclear reactors *via* the $^{235}U(n, \gamma)^{236}U$ reaction [7] (with a cross section of 95 barns for thermal neutrons *vs*. a fission cross section of 586 barns) and, to a lesser extent, by the alpha decay of ^{240}Pu. Thus, the determination of uranium concentration (using the isotope dilution technique) and burn-up of irradiated nuclear fuel in contaminated soil samples is also possible *via* the measured isotope ratios of uranium ($^{236}U/^{238}U$ and $^{235}U/^{238}U$). Accelerator mass spectrometry (AMS) [3–5] and thermal ionization mass spectrometry (TIMS) [5] are well established techniques for uranium isotopic measurements but these methods are expensive and sample preparation is time consuming. Inductively coupled plasma mass spectrometry (ICP-MS) provides high sensitivity, good accuracy of isotopic measurements, and a relatively simple sample preparation procedure [8, 9] and, therefore, is one of the mostly suitable methods for routine uranium isotopic ratio determination in environmental samples.

The aim of this work was the determination of the average burn-up values of irradiated uranium in contaminated soils collected at 11 sampling sites within a 30-km unpopulated area around Chernobyl NPP and at one sampling site near Choiniki, situated 53 km to the north of the Chernobyl NPP by using uranium isotopic measurements. The data obtained will be used to define more exactly levels of contamination with irradiated uranium and other radionuclides in the investigated areas.

Experimental

Samples

Soil samples were taken 4–53 km to the north and west of Chernobyl NPP (Fig. 2) in areas undisturbed by technogenic and anthropogenic activities since the Chernobyl accident. Soil was sampled with a coring device that was specially designed to cut 10 cm thick soil layers down to 60 cm. The collected soil samples were sieved through a 1.0 mm screen for the removal of stones and fragments of plant roots, and carefully mixed; then the samples were dried to constant weight at 105 ± 5 °C. After homogenization, 250 g of the sample was incinerated at 600 ± 50 °C for 1 hour. Plant roots and vegetation were incinerated separately at 550 ± 50 °C in an oven with oxygen supply for 2 hours and then the ash was mixed with the sample. Then the sample was leached with 9 M HCl. It was shown by Mironov *et al.* [10] that uranium originating from Chernobyl reactor is preferably extracted from soil samples into liquid 9 M HCl medium in comparison to the natural uranium in the hexavalent state. Therefore, this approach allowed partial isolation of reactor uranium for the following determination of its burn-up. After leaching by HCl, uranium was extracted by ion-exchange chromatography using anionite resin AB-17 (Joint Stock Company Azot, Novomoskovsk, Russia) and extraction with diethyl ether [10].

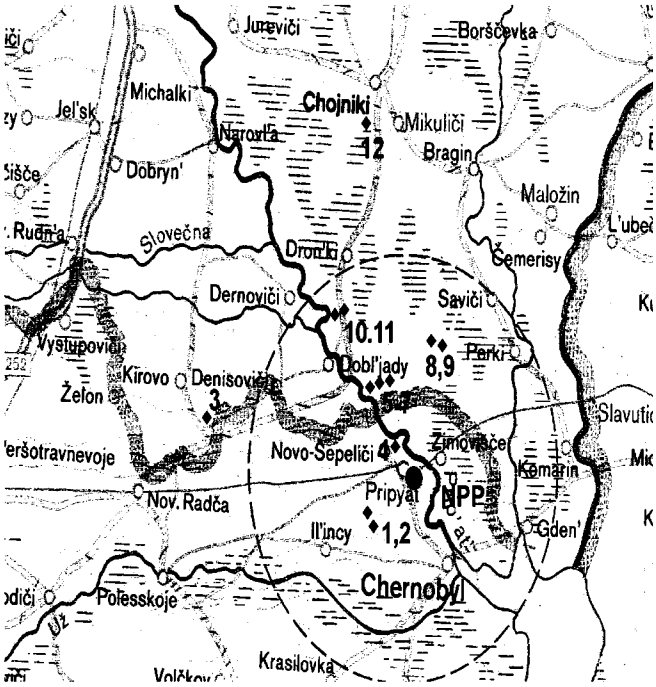

Fig. 2. Map of the sampling sites in the Chernobyl vicinity.

The concentration of uranium in the soil samples was measured by parallel analyses of the same samples using isotope dilution with ^{233}U (^{233}U abundance of 99.9%) as isotope spike. 2 g of the incinerated soil sample was spiked with a known quantity of ^{233}U tracer isotope and digested in a microwave oven with a mixture of nitric acid and hydrofluoric acid. The solution was evaporated, the residue was boiled on a hot plate with concentrated $HClO_4$, evaporated again, and then dissolved and separated by ion-exchange chromatography as described above.

Instrumentation and measurement procedure

A double-focusing sector-field inductively coupled plasma mass spectrometer (ICP-MS ELEMENT, Thermo Electron, Bremen, Germany) with a low-flow microconcentric nebulizer (MCN) with membrane desolvator (Aridus, CETAC Technologies Inc., Omaha, Nebraska, USA) [8, 9] was used for isotopic ratio measurements of uranium in aqueous solution after digestion of soil sample and chemical separation of uranium.

An isotopic standard solution of uranium (CCLU-500 laboratory standard, Nuclear Research Center, Prague, Czech Republic [11]) was used for optimizing isotope ratio measurements of uranium. Uranium solution with natural isotopic composition was prepared as described elsewhere [12]. All reagents were diluted with deionized Milli-Q water (18 MΩ) obtained from a Millipore Milli-Q-Plus water purifier to the necessary concentrations for determining the isotopic ratios of uranium by ICP-MS. The solutions were acidified to with 1% subboiled HNO_3. Optimization of the experimental parameters of ICP-SFMS was performed with respect to the maximal ion intensity of $^{238}U^+$ and minimal uranium hydride formation rate using a 1 $\mu g\,l^{-1}$ natural uranium solution introduced by the MCN with Aridus desolvator. The measured uranium isotopic ratio in soil samples

was corrected taking into account the mass discrimination factor, assuming a linear correlation [13, 14] determined experimentally by measuring CCLU-500 standard solution as well as hydride rate UH^+ ratios and the dead time of the detector of the ICP-MS [15]. The combined uncertainty of isotopic ratio measurements was calculated according to the EURACHEM/CITAC Guide [16] taking into account standard deviations of the measured ratio, background (including instrument background and interfering hydride ions) uncertainties of mass discrimination factor and the dead time and uncertainty associated with uranium isotopic standard.

Method for determination of burn-up and concentration of irradiated uranium

The burn-up and concentration of irradiated uranium in soil samples was determined by using experimentally measured $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios and calculated correlation coefficients between uranium isotopes in the reactor core, which depend on the burn-up of irradiated uranium.

A detailed analysis of the dependence of the isotopic composition of nuclear fuel (^{235}U, ^{236}U, ^{238}U,^{239}Pu, ^{240}Pu *etc.*) on burn-up in different reactors is performed in [17]. For RBMK (Chernobyl-type) reactors, some differences in concentrations and isotopic compositions of the radionuclides produced can take place even at the same burn-up depending on the location of fuel in the reactor core. These differences are mainly due to the changing of the coolant density with the height of the technological channels and variations of the neutron spectrum in different zones of the reactor core.

Taking account of the neutron-physical parameters of the Chernobyl reactor (design peculiarities of fuel assemblies, coolant density *etc.*) the neutron spectral density distribution was evaluated in the reactor core and the concentration ratios of ^{236}U, ^{235}U and ^{238}U isotopes were estimated as functions of burn-up with a relative uncertainty of less than 5% with respect to the whole range of possible coolant densities and local peculiarities of neutron spectra in different reactor core zones.

Based on these data, determination of burn-up B was performed from the following approximated equation:

$$154B^{-1.346} - 4180\delta B^{-0.817} = (\beta - \delta)/\alpha\,,$$

where $\delta = \rho_{5.0}/\rho_{8.0}$ is $^{235}U/^{238}U$ concentration ratio in natural uranium; $\alpha = \rho_{6,*}/(\rho_{8,0} + \rho_{8,*})$ and $\beta = (\rho_{5,0} + \rho_{5,*})/(\rho_{8,0} + \rho_{8,*})$ are measured $^{236}U/^{238}U$ and $^{235}U/^{238}U$ concentration ratios, respectively.

Spent reactor uranium concentration $\rho^* = \rho_{5,*} + \rho_{6,*} + \rho_{8,*}$ was calculated using the following equations: $\rho_{5,*}/\rho_{6,*} = 154B^{-1.346}$ and $\rho_{8,*}/\rho_{6,*} = 4180B^{-0.817}$. The above equations contain the following symbols: $\rho_{5,0}$ – concentration of ^{235}U originating from natural uranium in soil sample g/kg; $\rho_{5,*}$ – concentration of ^{235}U originating from irradiated uranium in soil sample g/kg; $\rho_{8.0}$ – concentration of ^{238}U originating from natural uranium in soil sample g/kg; $\rho_{8,*}$ – concentration of ^{238}U originating from irradiated uranium in soil sample g/kg; $\rho_{6,*}$ – concentration of ^{236}U originating from irradiated uranium in soil sample g/kg; B – burn-up, g/(kg U).

Results

^{236}U was detected in all soil samples collected to the north and west of Chernobyl NPP (resettlement area and some populated regions) at distances of 4 km to 53 km pointing to contamination with spent nuclear fuel. The occurrence of ^{236}U in soil samples is evidence for contamination due to nuclear fallout from the Chernobyl accident. As uranium with natural isotopic composition is mixed with spent reactor uranium in contaminated soil samples, the observed uranium isotope ratios deviate in a relatively wide range, *i.e.* the $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios range from 7.25×10^{-3} to 1.04×10^{-2} and from 7×10^{-7} to 1.2×10^{-3}, respectively (Table 1). The determination of $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotopic ratios by ICP-SFMS revealed the portion of nuclear fuel in the spent uranium/natural uranium mixture and provided information about the degree of burn-up of spent reactor uranium. Table 2 presents the results of cal-

Table 1. Variation of uranium isotope ratios in contaminated Chernobyl soil samples.

Isotope ratio	Chernobyl soil samples	In nature [6]
$^{234}U/^{238}U$	0.000055 –0.000117	0.000055
$^{235}U/^{238}U$	0.00725 –0.0104	0.00725
$^{236}U/^{238}U$	0.0000007–0.0012	$< 10^{-9}$

Table 2. Soil types at sampling sites, measured concentrations of irradiated uranium and its burn-up in upper 0–10 cm soil layer (sampling points 1–3 are situated on the western Chernobyl fallout tail, sampling points 4–12 are situated on the northern Chernobyl fallout tail).

Sampling point	Name	Soil type	Distance, km	Concentration of irradiated uranium in soil, $\mu g\,g^{-1}$	Burn-up, MWd/(kg U)
1	Chistogalovka	turf-podzol, sand-clay	7	0.76	9.3
2	Chistogalovka	Peat	7	2.0	9.1
3	Hatki	turf-podzol, sand	24	2.1×10^{-3}	9.2
4	Pripyat	Sand	4	0.81	9.3
5	Masany	turf-podzol, sand-clay	12	0.78	9.9
6	Masany	turf-podzol, sand-clay	12.5	2.5×10^{-2}	9.3
7	Masany	Peat	12.5	1.2	9.6
8	Kulazhin	turf-podzol, sand	18	6.3×10^{-3}	9.2
9	Kulazhin	Peat	18	4.3×10^{-3}	9.3
10	Lesok	turf-podzol, sand	24	2.7×10^{-2}	9.4
11	Lesok	Peat	24	1.2×10^{-1}	9.4
12	Chojniki	turf-podzol, sand-clay	53	1.3×10^{-2}	7.7

culating the concentration of irradiated reactor uranium in soil samples and its burn up at 12 sampling sites. Sampling sites 1–3 were selected on the western fallout tail and points 4–12 were selected on the northern fallout tail injected from the damaged Chernobyl reactor. The concentration of Chernobyl spent uranium in the upper 0 cm–10 cm soil layers in areas investigated in the vicinity of Chernobyl NPP amounts to 2.1×10^{-9} g/g to 2.0×10^{-6} g/g, depending mainly on the distance from the Chernobyl reactor. In general, the portion of spent uranium decreases with increasing distance from the Chernobyl NPP and the highest concentrations of spent uranium were observed in soils within radioactive spots closest to the Chernobyl NPP (Chistogalovka, Pripyat, Masany).

The calculated burn-up of reactor uranium in all soil samples within the 30-km area around the Chernobyl NPP was similar and the average value amounted to about 9.4 ± 0.3 MWd/(kg U). This value is about 17% lower than the average burn-up over the reactor core calculated by Begichev *et al.* [1] In the Choiniki area, a lower burn-up of 7.7 MWd/(kg U) was observed. It should be mentioned that the concentration of irradiated Chernobyl uranium in Choiniki was relatively low, and therefore, the uncertainty of the burn-up determination was greater.

Conclusion

$^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotope analysis in soil samples after digestion and analyte separation by ICP-SFMS allowed the determination of the concentration of irradiated reactor uranium in the reactor/natural uranium mixture and the estimation of reactor uranium burn-up. The measurement of uranium isotope ratios provides direct information on the burn-up of spent uranium in contrast to calculation methods based on isotope ratios of fission products (*e.g.* $^{134}Cs/^{137}Cs$ isotope ratio).

A slight variation of the burn-up grade of irradiated uranium was observed in this work. In particular, the burn up of reactor uranium in soil samples collected outside the 30-km area around the Chernobyl NPP differed from the burn-up value in soils samples collected close to the destroyed reactor. Within the 30-km area, the burn-up was similar on both western and northern fallout tails. Therefore, the same correlation coefficients for transuranium radionuclides originating from the destroyed Chernobyl reactor can be used for all investigated regions within the 30-km area, but outside this area the correlation coefficients might differ.

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