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CHEMICAL PERSPECTIVE ON RADIONUCLIDE EMISSIONS AS ATMOSPHERIC CONTAMINANTS FROM NUCLEAR REACTORS

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Abstract. This study investigates the radionuclide emissions from nuclear power plants (NPPs), focusing on the gas-aerosol emissions from reactors such as VVER-440. The radionuclide composition of these emissions is analysed to determine the biological hazards they pose, particularly focusing on isotopes such as tritium and radiocarbon. The research highlights the patterns of radionuclide accumulation in fuel assemblies using "rank-size" coordinates, which provide a more visual and informative method compared to traditional atomic weight dependency analyses. The study introduces the Zipf-Mandelbrot type rank distributions and proposes that the emissions can be effectively monitored by measuring only a few key radionuclides, thereby simplifying the process. This method is validated across different reactor types, indicating its broad applicability. The research underscores the potential of using these patterns for more efficient regulation and control of radionuclide emissions from NPPs.

Keywords: radionuclide, NPP gas-aerosol emission, Zipf distribution, rank distribution, radioactive emission, fingerprint criterion.

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Introduction

The regulation of atmospheric emissions of the most active radionuclides during the operation of NPPs and the determination of the total dose impact on the population is given serious attention, and its procedure is constantly being improved and refined [1]. The radionuclide composition of gas-aerosol emissions from NPPs with VVER-440, VVER-1000, and RBMK-1000 reactors into the atmosphere at the zero approximation corresponds to the composition of the fuel operating in the reactor.

This paper is focused mainly on analysis of the composition of spent fuel from water-cooled reactors. VVER reactors are the most frequently built type of reactor in the world. Currently 23 units of VVER-440 and 28 units VVER-1000 are operating all over the world. A detailed description of the design and technical scheme of Russian reactors VVER-440 and VVER-1000 is given in [2]. The most important design features of VVER-type reactors are:

- hexagonal geometry of the fuel assembly with the arrangement of fuel elements in a triangular lattice;
- zirconium-niobium alloy as fuel rod cladding material;
- possibility to transport all large equipment by rail to ensure full production process in factory conditions (which leads to limitation of outer diameter of reactor vessel);
- original design of horizontal type steam generators with a tube sheet in the form of two cylindrical heads.

The first units with predecessors of VVER-440 type reactors were erected at the Novovoronezh NPP site in 1972 and 1973. The second step in the development of VVER-440 reactors was the V-230 design, where the number of mechanical control rods was reduced from 73 to 37 due to the introduction of boron as a moderator. In the period from 1973 to 1982, all 14 blocks were built according to the V-230 design. The third stage of VVER-440 development was the V-213 reactor design, called the second generation of standard VVER-440 reactors; they are based on double-sided instantaneous guillotine rupture of the main pipeline of maximum diameter.

The development of VVER-1000 reactors began in 1966. The first reactor with an electric capacity of 1000 MW was commissioned at the Novovoronezh NPP in 1980. The design used traditional VVER engineering solutions with appropriate modernization from the experience

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gained in the design, manufacture and operation of VVER prototypes.

The design concept was oriented on improving the economic efficiency of the construction and operation of a nuclear power plant (NPP), ensuring safety in accordance with the regulatory documents in force at that time.

The experience of operating nuclear power plants with VVER reactors since 1964 confirms that the steps taken to ensure their safety were in the right direction [3]. The yield of radioactivity from nuclear power plants and the radiation dose in their premises are significantly lower than the permissible values. The operation of nuclear power plants with VVER reactors did not affect the levels of radioactivity measured near them. The only cases of leaks in the primary circuit were compensated by backup water supply at a pressure close to the nominal one. Large-scale measures to ensure the safety of nuclear power plants with VVER reactors under construction and design currently correspond to their increasingly widespread use in the USSR power system.

As for RBMK reactors, after the Chernobyl disaster, the operating RBMK reactors were improved, taking into account the experience of the disaster. Today, nine RBMK reactors are still operating. All of them are located in Russia [4]. Concerning the safety of such type of reactors, one can read very peculiar published materials [5,6].

It should be emphasized that, from a biological hazard perspective (primarily for humans), the emissions of tritium (^{3}H) and radiocarbon (^{14}C) compounds, as elements that are part of biological tissues, are among the most dangerous [7]. At the same time, these light elements (as well as argon isotopes) are not fission products of uranium, meaning they accumulate not in the fuel assemblies themselves but in the environments directly contacting the reactor, including the atmosphere and coolants. These are products of induced radioactivity arising from the irradiation of previously non-radioactive elements with ionizing radiation, especially neutrons. When irradiated by particles (neutrons, protons), stable nuclei can be transformed into radioactive nuclei with varying half-lives, continuing to emit radiation long after the irradiation ceases. Nuclear reactors operate for extended periods (tens of years) under intense neutron irradiation (the neutron flux intensity in some power reactors reaches 10^{16} $cm^{-2}\cdot s^{-1}$, and in some experimental reactors—even 10^{19} $cm^{-2}\cdot s^{-1}$), with a total fluence over the entire time reaching 10^{23} $cm^{-2}\cdot s^{-1}$ [8]. The neutron fluxes in projected thermonuclear reactors will be even more intense. This creates problems with the disposal of reactor structures. Naturally, the dynamics of the accumulation and consumption of induced products are described by a completely different model compared to the model for the accumulation of fission products. Its consideration is beyond the scope of this publication, which primarily focuses on isotopes in the mass number range of 70 to 160.

It is known that under neutron irradiation of the fuel material (a mixture of ^{238}U and ^{235}U isotopes), fission of ^{235}U atoms into two fragments of different masses occurs [9], contained in the spent fuel at a certain concentration. However, as shown in the previous article [14], there is no clearly expressed pattern and analytically representable relationship between the mass yield (concentration) of radionuclides and their atomic mass, which practically excludes the possibility of constructing simple predictive models based on mass distribution (or atomic number, which, from a modelling perspective, is the same). The resulting fragments are also generally subject to radioactive decay. Within this work, it is hypothesized that, unlike concentration, their decay rate will follow known physical rules. Physical rules imply the possibility of applying sufficiently rigorous mathematical analysis.

The purpose of this work is to demonstrate, using the VVER-440 reactor as an example, the sufficiency of normalizing the total dose of emissions into the atmosphere with a sample of a group of five (maximum - ten) of the most active radionuclides to identify the entire spectrum of radioactive emissions, similar to a "fingerprint."

Research methodology

The statistical approach has been used as the main mathematical method of data treatment. An informed understanding of the patterns of accumulation of radioactive products in fuel assemblies can be achieved if the data are represented in coordinates that are somewhat unusual for physics but widely used in economic and social statistics. The speech is about so-called distributions with "heavy tails", where deviations from the average value by several orders of magnitude in either direction can occur with a non-zero probability. Recall that deviations beyond "three sigmas" for normal Gaussian distributions are considered practically impossible [10].

For convenience in representing data with wide distributions, "rank - size" coordinates are used. In this case, the rank refers to the ordinal number of the value in a sample ordered by total emission ("size"): the most representative element is assigned rank 1, the next 2, and so on, decreasing

to the smallest object according to the studied indicator. The term "size" adopted for such distributions is not entirely successful as it does not fully describe the essence of the approach. Depending on the goal, the data can be ranked by a wide range of indicators, with ordering by quantity being not the only possible option. In this case, the abscissa on the graph will be the ordinal number in the ranked sample, and the ordinate can represent the probability, frequency of occurrence, or quantity of objects corresponding to the rank. Apparently, if instead of the shortened term "size", is used its expanded form "size of the sample of this rank" or "fraction size", the misunderstanding disappears. A fairly strict and detailed description of rank distributions can be found, for example, in [11]. At a popular level, which is sufficient to understand the main features of the approach, one can limit oneself to the reference [12]. In some cases, "rank" dependencies turn out to be more visual and informative than the dependencies of one physical quantity on another.

Results and discussion

To compare, the distribution of mass yield and the distribution of activity should be considered not as a function of the atomic weight of the radionuclide fragment (*i.e.*, mass number) but as a function of its rank. For this purpose, it is necessary to arrange the complete sample of 522 radionuclides presented in [9] according to their contribution to activity (method 1) or to the mass composition (method 2) of spent fuel (Figures 1–4). The corresponding distributions are shown in Figures 1 and 3 in regular coordinates and in Figures 2 and 4 in semi-logarithmic (ordinate) coordinates.

For activity, the rank distribution is generally close to hyperbolic, i.e., the "representativeness" of a radionuclide is inversely proportional to its rank (Eq.(1)).

$$A(k) \sim \frac{1}{k} \quad (1)$$

where, *A(k)* is the activity of the radionuclide;
k is the rank of the radionuclide.

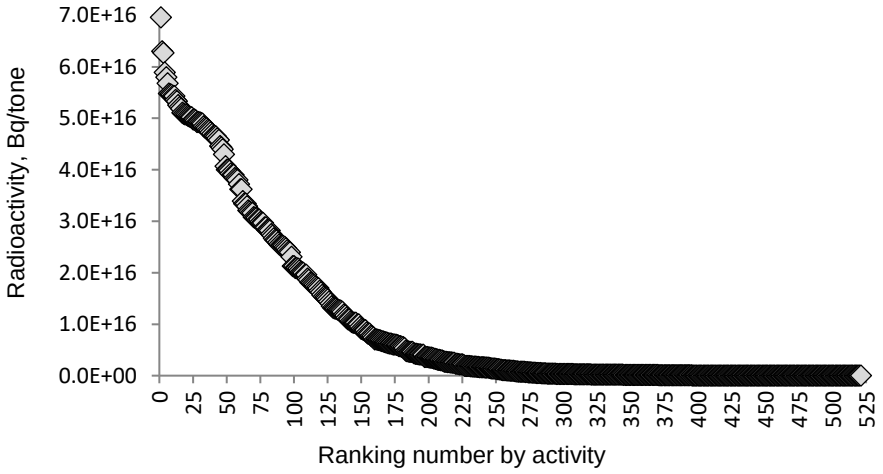

Figure 1. Decline in the activity of fission products depending on the rank of the radionuclide.

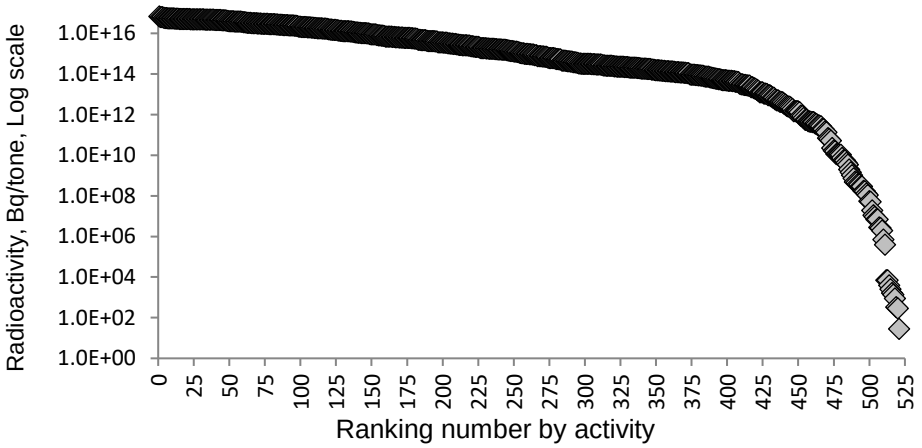

Figure 2. Decline in the logarithm of the activity of fission products depending on the rank.

For rank distributions, this dependency is known as the "Zipf-Mandelbrot distribution" [12,13]. In logarithmic coordinates, the inverse proportionality would reduce to a straight line, but as seen in Figure 2, after the 400th rank, the dependency noticeably declines, which, however, is insignificant for the overall picture.

The next two Figures 1 and 2 demonstrate the rank distribution of the mass yield (concentration) of spent radionuclides.

The usual representation (Figure 3) is provided only to demonstrate that mass yield heavily depends on rank. However, the graph itself is not very informative; instead, it makes sense to analyse the logarithmic representation (Figure 4). It has a characteristic S-shape, suggesting a log-normal type of distribution by mass yield.

To check how accurately the log-normal distribution of radionuclides by mass yield is followed, a histogram of mass yield for fission fragments can be constructed. For this purpose, the entire scale of yield values can be divided into a certain number of "bins." In the case of this study, such bins can be values of the decimal logarithm of the number of atoms in a unit of spent fuel weight [10]. For a quantity of 1 to 10 atoms (the decimal logarithm of the right boundary is 1), it is proposed to assign bin number 1, the next bin number 2 will collect representatives with a yield of 10 to 100 atoms, and so on. Since no isotope will be represented by a number of atoms higher than 10^{30}, one can limit ourselves to 30 bins. The corresponding histograms are shown in Figure 5 (differential) and Figure 6.

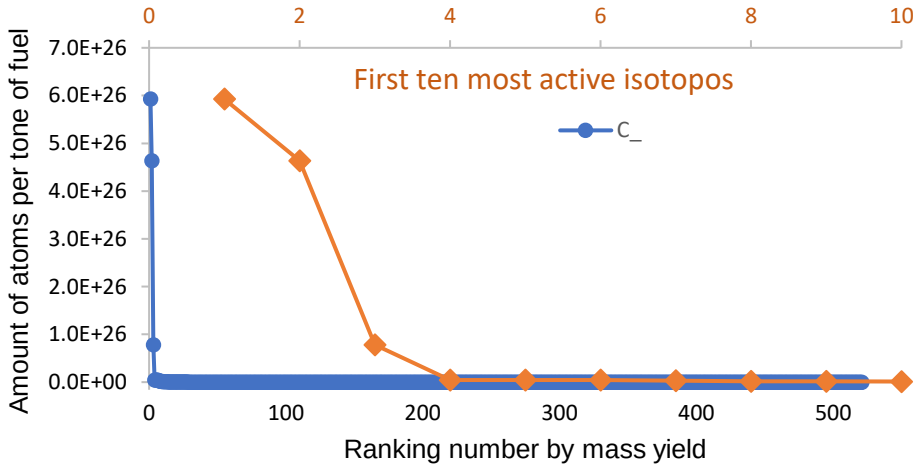

Figure 3: Mass yield for fission products in VVER-440 depending on the rank. The red curve refers to the upper horizontal axis and shows the decline for the first 10 elements.

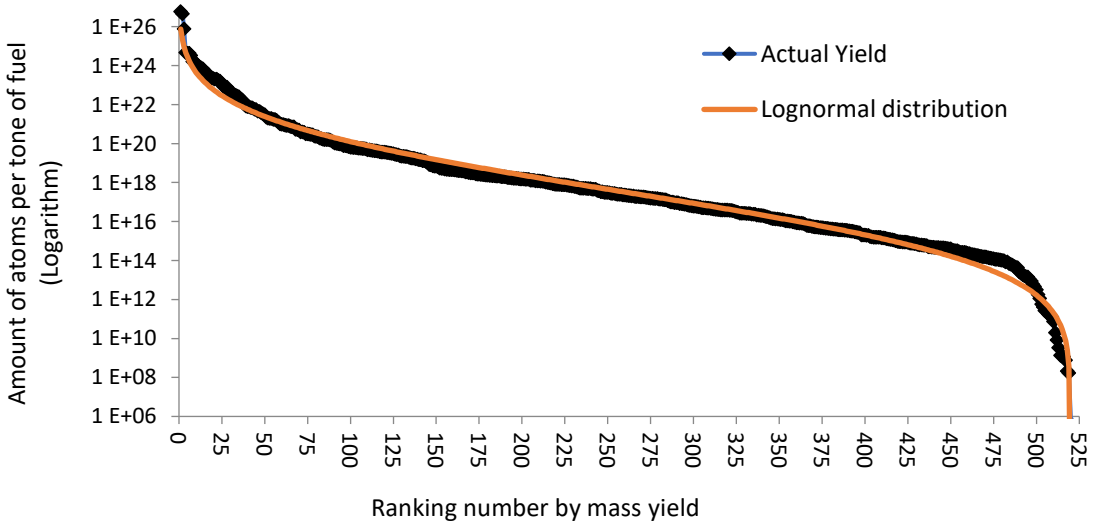

Figure 4. Logarithmic representation of mass yield for fission products in VVER-440 depending on the rank. The red line shows fitting with log-normal distribution.

It can be noted that the graph of the log-normal distribution in Figure 6 is essentially a variation of the graph in Figure 4 obtained by transposing the axes. A more interesting observation is that the log-normal distribution is characteristic of a wide variety of fragmentation processes. The statistical theory of solid material fragmentation begins with the classic work of Kolmogorov, A.N. [13], in which it was proposed to describe the state of each fragment of a system by a single parameter - the generalized size R. Based on simple and very transparent assumptions, a probabilistic model was constructed, describing the system's evolution in a discrete time scale. On this basis, the final probability distribution for random fragment sizes was found in the form of a log-normal distribution. One of Kolmogorov's key assumptions is the scale invariance of the fragmentation mechanism, which consists of the invariance of all relations when replacing $R \rightarrow \lambda R$. Subsequently, Kolmogorov's model was developed in various directions.

According to the ideas suggested in the actual study, a nuclear reactor can be imagined (purely hypothetically for the sake of realizing the mathematical model) as a kind of ball mill. Just as finely ground products with a normal distribution of the logarithm of size are formed in the mill, in the reactor, the release of each isotope can be associated with a cluster corresponding to the number of atoms of this isotope. The size of the cluster, or the logarithm of the cluster size, is a random variable with a Gaussian (normal) distribution, following the log-normal distribution.

It should be emphasized that the cluster approach provides the possibility of describing NPP gas-aerosol emissions using known mathematical regularities, whereas attempts to link to atomic weight, atomic number, or any other physical characteristic of the radionuclide do not allow for mathematical analysis. In this sense, the cluster size is a full analogue of the rank by "representativeness" in the mass emission of a given isotope among all isotopes.

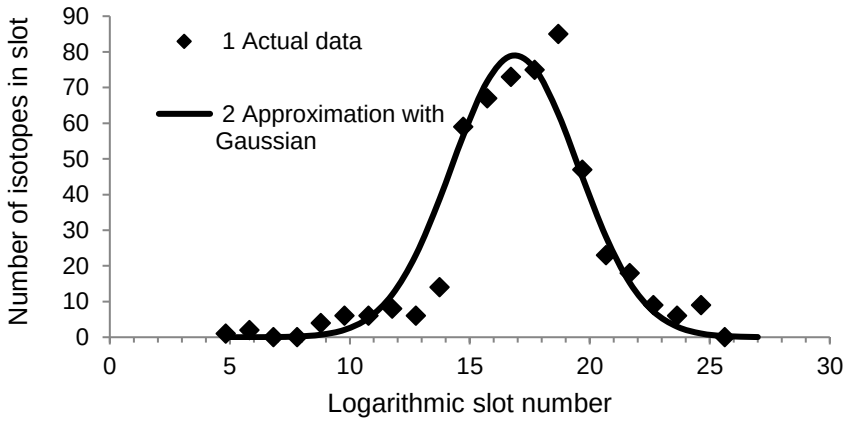

Figure 5. Differential histogram of mass yield for fission products in VVER-440.

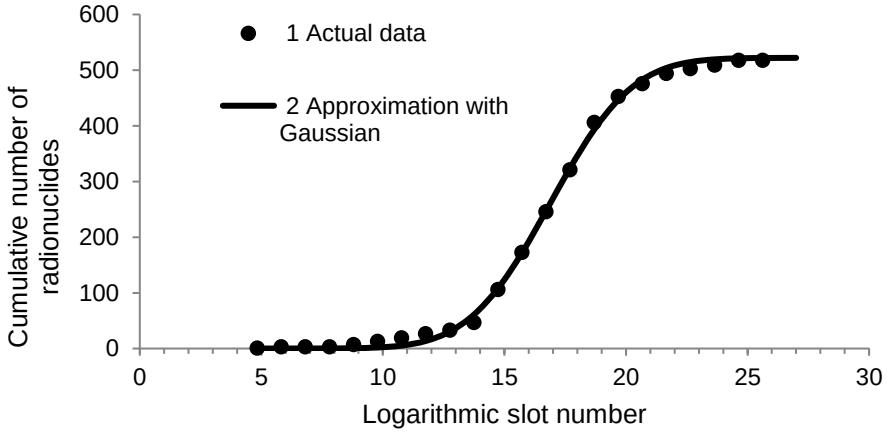

Figure 6. Cumulative (integral) curve of mass yield for fission products in VVER-440 depending on the "bin number".

In authors' opinion, experimental confirmation of the log-normal distribution of radionuclides by "cluster size" is of not only fundamental interest but also important practical significance, as it allows for a significant reduction in the volume of necessary measurements for normalizing the total dose of emissions into the atmosphere.

In fact, having a log-normal (or any other but constant-form) distribution function allows us to conduct measurements not for all isotopes but only for a few that are most convenient to measure. The selection of five well-known radionuclides presented in [8], similar to a "fingerprint," allows the identification of the entire spectrum of radioactive emissions. Naturally, for a complete picture, it is necessary to add at least predictive calculations for tritium and radiocarbon, but they require the development of a separate model. At the same time, to get a general picture of uranium fission products, it is sufficient to have data on the most representative high-ranking radionuclides to extrapolate them to the entire family. It is not accidental that IRG and the cesium-iodine group are chosen for control and normalization. They correspond to the first peak (krypton) and the second (xenon, cesium, iodine) on the well-known "two-humped" radionuclide yield curve.

A crucial question constantly arising before organizations exercising control and supervision over radioactive emissions concerns the possibility of compiling a "short list" of radionuclides that would be responsible for 95% (or 99%, or 90%) of the total dose load on the territories adjacent to the NPP.

Given the broad (non-Gaussian, but log-normal) nature of the distribution by activity, such a question is practically unsolvable. The graph in Figure 7 clearly shows that the twenty most active radionuclides contribute only about 20% to the total activity, and the first 50 most important radionuclides correspond to less than half of the total activity. For this reason, the attempt to directly control 95% of the radioactive background would require establishing standards for hundreds of isotopes, which would increase the labour intensity of existing radiometric procedures by orders of magnitude. As the materials of the publication indicate, such total control is completely unnecessary. Knowing the distribution functions and having sample measurements for five to ten authorized radionuclides, a comprehensive picture of the composition and volume of all radioactive emissions can be defined.

Currently, the authors are working on applying machine learning methods and neural networks to identify functional dependencies of emission activity into the environment that are difficult to express in the form of an analytical formula. There is reason to believe that the developed methodology will be somewhat simpler than the one presented in [8]. At the same time, to maintain the reliability of calculating permissible emissions, it is also necessary to link them with the calculation of dose loads on biota.

Regarding the effect of radioactive aerosols on human, animal and plant health in the environment, the number of published works is quite significant, see for example [15-18]. However, consideration of the biomedical aspects of the problem goes far beyond the submitted work.

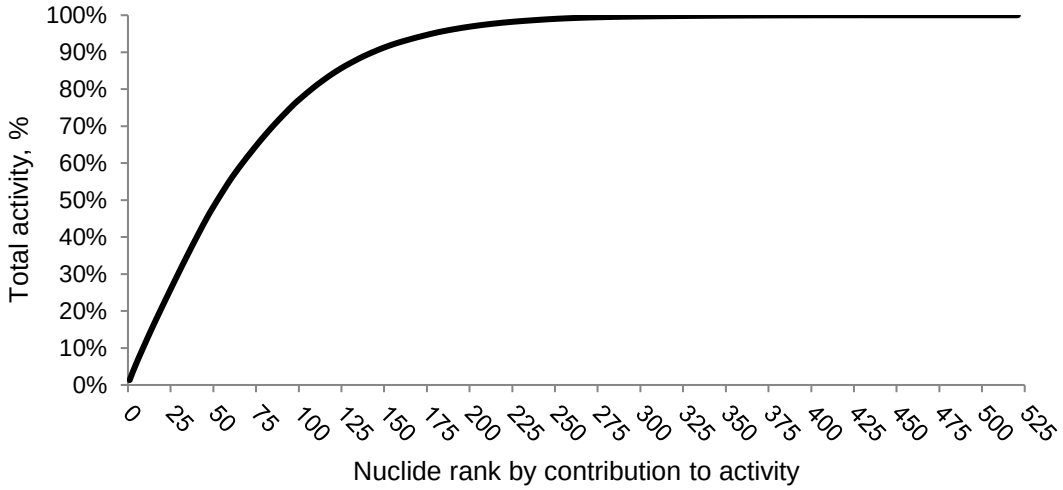

Figure 7. Percentage of total activity of the radionuclide sample depending on the number of isotopes considered (based on tabular data from [2]).

Conclusions

A hypothesis is proposed: the primary (before the use of filters and gas purification systems) radionuclide composition of gas-aerosol emissions from nuclear power plants with VVER-440 reactors into the external environment corresponds to the composition of the fuel operating in the reactor.

It is shown that the applied method of studying the patterns of accumulation of radioactive products in fuel assemblies, based on the presentation of data in the coordinates "rank - size," turns out to be more visual and informative than the traditionally accepted analysis of dependencies on atomic weight. The transition to Zipf-Mandelbrot type rank distributions presents fundamentally new analytical prediction possibilities.

It has been shown that in the reactor, the operating time of each isotope can be compared to a cluster corresponding to the logarithm of the number of atoms of this isotope. The log-normal distribution obeys the cluster size, which has a Gaussian distribution after assigning isotopes to "logarithmic pockets".

Using the log-normal distribution function, it is possible to control emissions for only a few radionuclides that are most convenient for measurement. A sample of the five most active radionuclides, like a fingerprint, allows you to identify the entire spectrum of radioactive emissions.

The analysis of the composition of irradiated fuels of reactors VVER-1000 and RBMK-1000 showed that the obtained patterns are fulfilled for them to the same extent and with the same accuracy as for reactor VVER-440, for which data processing is given.

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