CHARACTERISTIC FEATURES OF THE RADIOLYSIS OF WATER IRRADIATED UNDER STRICTLY FIXED CONDITIONS AND UNDER CONDITIONS VARYING OVER A SMALL RANGE

M. L. Lukashenko, S. A. Kabakchi, O. P. Arkhipov, and A. I. Milaev

A qualitative mathematical analysis of the system of differential equations that describes the radiolysis of pure water and water solutions of hydrogen, hydrogen peroxide, and oxygen is performed. It is established that in a closed volume with fixed values of external parameters (dose rate, temperature, and others) a steady state characterized by a stable singular point-type attractor is unavoidably reached. The type of attractor does not depend on the values of the external parameters, i.e., in principle the system possesses self-regulation properties with respect to them. It is shown that under real conditions, when the external parameters cannot be strictly fixed, the existence of a stationary state and a stationary concentration of the products of radiolysis of water are determined not only by the specific values of the external parameters but also by their variation in the time required to establish a stationary state. 3 figures, 1 table, 10 references.

The principle of internally inherent self-shielding is widely used in safety design of modern nuclear reactors. The crux of this principle is that in an accident negative feedbacks due to the physicochemical properties of systems, and not dependent on the actions taken by the operators, appear. Examples are a decrease in criticality accompanying the evaporation of coolant in the reactor core in a loss-of-coolant accident in installations with VVÉR reactors or a decrease in the density of the water solution of uranyl sulfate in the fuel tank as a result of radiation-chemical release of gas accompanying uncontrolled growth of the reactivity of a homogeneous reactor.

The water-chemical regime of the fast loop of a VVÉR reactor, which represents the technology for suppression of radiolysis of water, reducing corrosion of equipment to a minimum, and decreasing the quantity of radioactive deposits in the loop, in light of the concept of deep-layering of shielding [1] is one level of shielding of a reactor installation. The method for solving these problems is to introduce into the coolant chemical additives that produce in the first loop a reducing medium and maintain a standard pH. Ammonia is ordinarily used as such an additive in VVÉR reactors. In the core, ammonia decomposes under the action of ionizing radiation at high temperature into molecular hydrogen and nitrogen. The hydrogen form suppresses radiation-chemical generation of oxygen, and it decreases the concentration of oxygen that has entered the coolant with the makeup. It is known that in water solutions of a mixture of nitrogen and hydrogen the reverse process—synthesis of ammonia—is also possible under the action of radiation. This means that under certain conditions a radiation-chemical stationary state, in which the rate of decomposition of ammonia is equal to the rate of synthesis of ammonia and the concentration of all coolant components remains constant for indefinitely long time, can exist in the coolant. In such a regime ammonia needs to be added to the loop only to compensate for the losses of ammonia with coolant leaks.

1 Russian Science Center "Kurchatov Institute."
3 OKB "Gidropress."

Under laboratory conditions, where in experiments the external parameters (dose rate, temperature, rate of entry and exit of reagents, and others) can be maintained constant to a high degree of accuracy, it is easy to find conditions under which a stationary state is realized and then to maintain the system in this state. In practice, for example, for radiolysis of the water coolant in the first loop of a VVER reactor, the external parameters can vary either randomly or for technological reasons. Such a change in the system parameters should result either in the modification of the stationary state or cause the state to vanish. However, it can be conjectured that for each specific system there is a range where variation of the external parameters does not destroy the stationary nature of the radiolytic process. The search for such regions is interesting from the theoretical and practical standpoints. In the later case, regulated holding of the external parameters in the regions found actually means realization of a self-regulated water-chemical regime.

In the present work we examine in a general form the conventional mechanism of radiolysis of water and its mathematical description as a whole in order to determine the properties characteristic of such a complicated system and its behavior under real conditions, for example, in the first loop of a VVER reactor. This methodology was first used to analyze thermal explosions [2] and is widely used to study catalytic processes [3]. It proposes the following: first, the construction of a hierarchy of processes and phenomena when analyzing the mechanism of chemical transformations; second, a qualitative mathematical analysis of the system of differential equations describing the dynamics of the variation of the coolant parameters in the ionizing radiation field; and, third, calculation of the kinetics of chemical transformations.

It can now be asserted that the general mechanism of radiolysis of water and solutions of oxygen, hydrogen, and hydrogen peroxide has been established. It has been proved experimentally that about 150 elementary reactions can occur under various conditions. The room-temperature rate constants have been determined for about 100 of these reactions and the activation energies have been found for more than 30 of the reactions. The general mechanism is described by a radical-diffusion model [4], which in the homogeneous approximation reduces to a system of ordinary nonlinear differential equations.

The general mechanism is widely used for practical purposes to predict radiation-chemical transformations in water under specific conditions, for example, in the first loop of a VVER reactor. There are two known approaches for predicting radiation-chemical transformations under specific conditions. Numerical simulation is most widely used. In this approach the general mechanism is reduced to the minimum number of reactions required to give a qualitative description of the process in a specific case. Next, a partial system of differential equations is constructed. The constant coefficients of this system are the radiation-chemical yield \( G_i \), the rate constant for elementary reactions \( k_i \), and the activation energy of the reactions \( E_i \). Some of them are known; the rest serve as degrees of freedom, making it possible to fit the solution of the system of differential equations to the experimental data obtained under conditions similar to those for which the prediction is constructed. After a fit is made, the mathematical model is assumed to be verified and suitable for prediction, which in this case consists of extrapolating the experimental data into the required range of external parameters without analyzing the admissability of such an extrapolation. In the other approach the general mechanism of radiolysis is not studied at all, but rather one or several "determining" elementary reactions are considered and the response of the radiation-chemical system, for example, the change in the concentrations of components under different actions, is predicted according to their behavior [5]. Without questioning the fruitfulness of either approach, it must nonetheless be recognized that they suffer from subjectivity, and their use for solving practical problems is based largely on the investigators intuition and is more an art than a field of exact science.

The approach to investigation of the radiolysis of water systems in which the general mechanism and its description are considered as a single whole is extremely rare. This is because the kinetics of radiolysis of water is described by a high-dimensional nonlinear system of differential equations, which is very difficult to analyze. At the same time, it must be acknowledged that the analytic approach is extremely fruitful. Examples are [6] concerning the analysis of the influence of the dose rate on radiation-chemical transformations in the liquid phase and the theoretical substantiation of the oxygen water-chemical regime of a RBMK reactor in the study of the material balance of the radiolysis of water [7]. We have undertaken a qualitative investigation, in general form, of the mechanism of radiolysis of water and the system of differential equations describing it. At the first stage, described in the present paper, the simplest case of radiolysis of neutral, clean water and dilute solutions of oxygen, hydrogen, and hydrogen peroxide in a system that is closed relative to mass-transfer but open for energy transfer is studied.

During the radiolysis of water radical and stable products are formed. We postulate the following reactions of the products of radiolysis, which are determined by their chemical nature and the law of spin conservation.

1. The interaction of any two radicals \( r_i \) and \( r_j \) gives only the stable product

\[ r_i + r_j \rightarrow X_L. \]