THE INFLUENCE OF MASS AND SIZE EFFECTS ON THE RADIOLYSIS PROCESS OF WATER IN THE BeO/H_2O SUSPENDED SYSTEM BY THE γ-QUANTA

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The amount, formation rate and radiation-chemical yield of molecular hydrogen obtained from water radiolysis process within the system, have been defined according to both water and BeO by maintaining the water volume constant (V = 5 ml); by changing the mass (m_{BeO}= 0.0 (pure water), 0.01; 0.02; 0.04; 0.08; 0.2 g) and particle size (d < 4, d = 32…53 and 75…106 μm) of beryllium oxide in the porous BeO/H_2O suspended systems by the influence of γ-quanta (^{60}Co, P = 19.5 rad/s, T = 300 K). It has been established that the amount, formation rate and radiation-chemical yield of molecular hydrogen defined according to both water and BeO from radiation-heterogeneous transformation of water in these systems, change depending on mass and particle size of BeO added to water.

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INTRODUCTION

Beryllium and its various compounds (beryllium oxide, ammonium fluorberillate, beryllium fluoride) are used as construction materials in the nuclear reactors (MTR, ETR, ATR, EBR-II, ITER) [1–3], as it has physical properties such as, high melting temperature, high thermal conductivity, small atomic mass unit, the ability to hold low hydrogen at high temperatures, low absorption and high reflection ability of heat neutrons, high elasticity modulus, chemical and corrosion resistance at high temperatures. These materials are exposed to the combined effects of temperature and ionizing radiation (neutrons, protons, γ-quanta, electrons, ά-particles, high-energy ions, etc.) in contact with water, which is used as a decelerator, retarder and energy carrier inside the reactor. Therefore, it is important to predict any changes in the operating mode inside the reactor, both for the safety of the reactor and for the transition into hydrogen energy in new-generation reactors.

For this purpose, researchers have begun to study extensively the process of radiation-heterogeneous transformation in heterogeneous systems created by liquid, gas, and especially water with nano- and micro-sized metals or metal oxides under the influence of ionizing radiation. In this regard, the dependence of the amount, formation rate and radiation-chemical yield of molecular products (H_2, O_2, H_2O_2, etc.), which are obtained from the radiation-heterogeneous transformation of water in metal or metal oxides/H_2O systems under the influence of γ-quanta, on their particle size has been observed in our [4-7] and some foreign authors' [8–16] studies. On the other hand, the radiation-chemical yields of products, obtained from water transformation in metal or metal oxide/H_2O suspended systems [6, 17, 18] under the influence of γ-quanta, were higher than in other systems.

Ouerdane H. and other authors have conducted the calculations [19] by modeling the process of electron transfer from the surface of silicon dioxide to water and vice versa in the physical and physico-chemical stages of the process under the influence of ionizing radiation on a system of amorphous silicon dioxide, suspended in water, by using the Monte Carlo method. It has been established that due to the electrons emitted into the water from the nanoparticle surface, the radiation-chemical yield of electrons solvated in water in a suspension system is higher than in pure water, and this ratio varies depending on the particle size of silicon dioxide.

This research has been conducted in two directions:

1. The suspension of metal or metal oxides in water by maintaining the water volume constant;
2. The adsorption of water on the surface of metal or metal oxides.

In each of these cases, radiation-chemical yields of products (H_2, O_2, H_2O_2, etc.) obtained from radiation-heterogeneous transformation of water,change depending on: their type, the band gap width, particle size, filling degree of the adsorbed water on the particle surface, total system temperature, the mass of metal and metal oxidessuspended in water.

Herein, it has been studied the influence of mass (m = 0.01; 0.02; 0.04; 0.08, and 0.20 g) and size effects (d < 4 μm, d = 32…53 and 75…106 μm particle size) on the amount, formation rate and radiation-chemical yield of molecular hydrogen obtained from water radiolysis in the systems of V = 5 ml bi-distilled water and BeO suspended through vibrator during radiation in the same amount water under the influence of γ-quanta (^{60}Co, P = 19.5 rad/s, T = 300 K).

EXPERIMENTAL PART

BeO with high purity (99.9%) and 60 m^2/g special surface, divided into d < 4 μm, d = 32…53 and 75…106 μm particle size by putting through a special sieve has been taken as a research object. After thermal treatment of the studied particle in the open air at a temperature of T = 773 K for t = 72 h, the required mass (m = 0.01; 0.02; 0.04; 0.08, and 0.20 g) was weighed and added to an ampoule (V = 19 ml) prepared from molybdenum glass, which is cleaned in a special mode and thermally treated (T = 773 K). BeO after 4 h of thermal treatment (T = 673 K) in vacuum (P = 10^{-3} mm c.st.) inside the ampoule, was cooled and sealed with V = 5 ml air-purified bi-distilled water [20].

The ampoule was irradiated at room temperature under special conditions (provided that the BeO particle

remained suspended in water by means of a vibrator during irradiation) at a source of ^{60}Co with a dose rate of P = 19.5 rad/s. The absorption dose rate was determined using ferrosulfate and methane methods. Absorption dose rate in a specific study object was calculated using electron density comparison methods [20, 21].

In the BeO/H_2O system, the final molecular products from the radiation-heterogeneous transformation of water were analyzed to be H_2, O_2, and H_2O_2. As some parts of O_2 were captured on the surface and H_2O_2 was in the solution, it causes great difficulties in determining their amounts. Therefore, more accurate information on the kinetic regularity of the products obtained from radiation-heterogeneous transformation of water was based on the amount of molecular hydrogen.

The reaction products were analyzed on "Agilent-7890" chromatograph. In parallel, a modernized "Tsvet-102" chromatograph (accuracy 8...10%) was used to confirm the results.A column with a length of 1 m and an inner diameter of 3 mm was used in the chromatograph "Tsvet-102". The activated carbon with a size of d = 0.25…0.6 mm and as a gas carrier argon gas with a purity of 99.99% on both chromatographshave been used inside the column.

OBTAINED RESULTS AND THEIR DISCUSSION

In Fig. 1, it has been given the dependence graphs of the amount of molecular hydrogen obtained from water transformation in the systems of V = 5 ml bi-distilled water (curve 1) and BeO with the particle size of d < 4 μm and mass of m (g) = 0.01 (2); 0.02 (3); 0.04 (4); 0.08 (5); 0.2 (6) suspended through the vibrator during irradiation in the same amount water under the influence of γ-quanta (^{60}Co, P = 19.5 rad/s, T = 300 K), on the irradiation period.

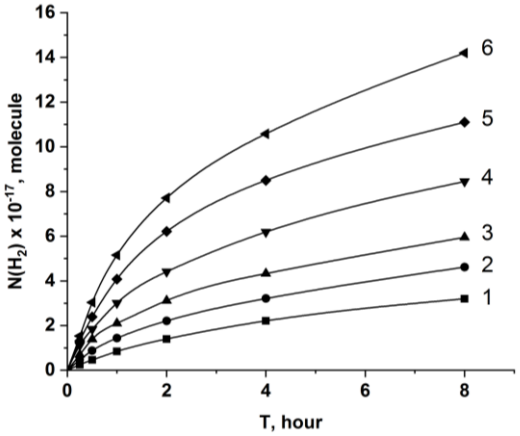

Fig. 1. Dependence of molecular hydrogen obtained from the water radiolysis in the systems of V=5ml bi-distilled water and BeO with the particle size of d<4 μm and mass of m(g) = 0.01 (2); 0.02 (3); 0.04 (4); 0.08 (5); 0,2 (6) suspended through the vibrator in the same amount water during the irradiation period under the influence of γ-quanta (^{60}Co, P = 19.5 rad/s, T = 300 K), on the irradiation period

In Fig. 2, it has been given the dependence graphs of the amount of molecular hydrogen, obtained from radiation-catalytic transformation of water in the systems formed by the addition of BeO with the particle size of d < 32…53 μm and d = 75…106 μm in the same condition in the Fig. 3 and mass of m (g) = 0.01 (1); 0.02 (2); 0.04 (3); 0.08 (4); 0.20 (5) in both cases, suspended through the vibrator during irradiation in V = 5 ml bi-distilled waterunder the influence of γ-quanta, on the irradiation period.

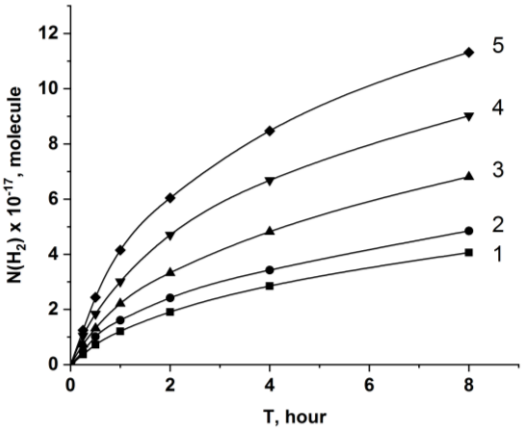

Fig. 2. Dependence of molecular hydrogen obtained from the radiation-heterogeneous transformation of water in the systems formed by the addition of BeO with the particle size of d < 32…53 μm and mass of m (g)=0.01 (1); 0.02 (2); 0.04 (3); 0.08 (4); 0.2 (5) suspended through the vibrator during the irradiation period in the V = 5 ml bi-distilled water under the influence of γ-quanta (^{60}Co, P = 19.5 rad/s, T = 300 K), on the irradiation period

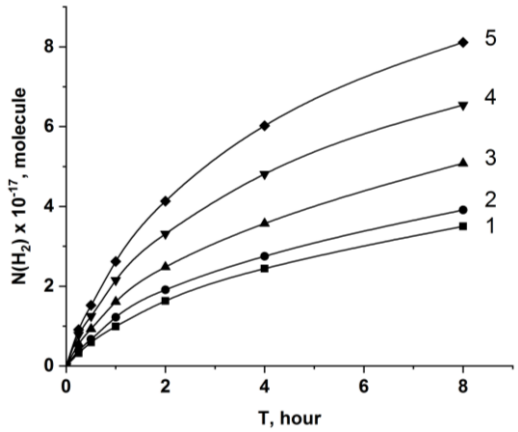

Fig. 3. Dependence of molecular hydrogen obtained from the radiation-heterogeneous transformation of water in the systems formed by the addition of BeO with the particle size of d < 75...106 μm and mass of m(g)=0.01 (1); 0.02 (2); 0.04 (3); 0.08 (4); 0.2 (5) suspended through the vibrator in the V = 5ml bi-distilled waterduring the irradiation period under the influence of γ-quanta (^{60}Co, P = 19.5 rad/s, T = 300 K), on the irradiation period

The formation rates of molecular hydrogen for both water and BeO – $w(H_2)$ and radiation-chemical yields according to these values – $G(H_2)$ have been determined from the kinetic parts of the graphs (Figs. 1–3). In the kinetic part of the graph, if the amount of molecular hydrogen obtained from the transformation of water during τ-irradiation period is $N_0(H_2)$, but it is $N(H_2)$ in the BeO/H_2O suspended system, then the formation rates of molecular hydrogen for water in both cases can

be defined on the basis of $w_0(H_2) = \frac{N_0(H_2)}{m_{water}t}$ and $w_{water}(H_2) = \frac{N(H_2)}{m_{water}t}$ expressions, respecttively, here, m_{water} – is the mass of water. Radiation-chemical yields of molecular hydrogen were determined on the basis of these rates. Based on the obtained results, it was given the dependence graphs of radiation-chemical yields of molecular hydrogen determined for water (Fig. 4) and BeO (Fig. 5), on its mass.

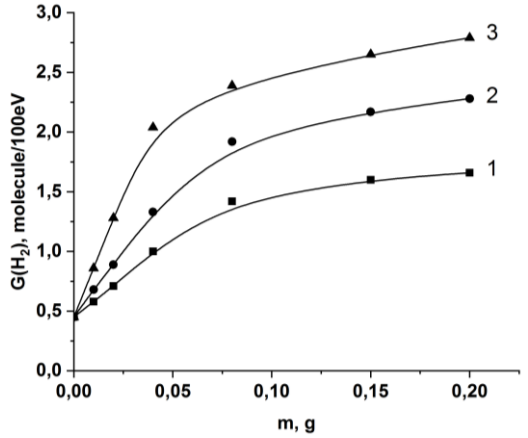

Fig. 4. The dependence of radiation-chemical yields of molecular hydrogen (which is obtained from water radiolysis in the systems formed by V = 5ml bi-distilled water and the addition of BeO particles with the size of d = 75…106 (1), 32…53 (2) and d < 4 μm (3) suspended through the vibrator in the same amount water during the irradiation under the influence of γ-quanta (^{60}Co, P=19.5 rad/s, T=300 K)), which are determined according to water, on its mass

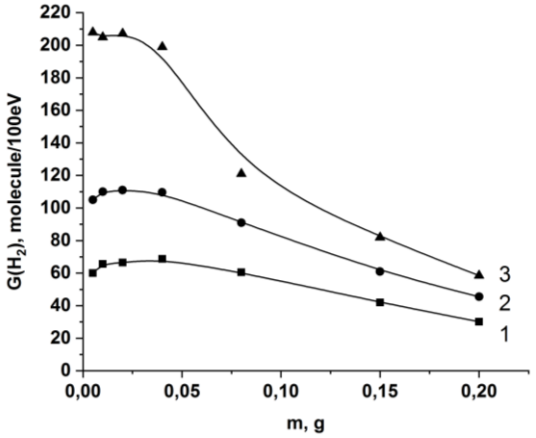

Fig. 5. The dependence of radiation-chemical yields of molecular hydrogen (which is obtained from water radiolysis in the systems formed by the addition of BeO particles with the size of d = 75...106 (1), 32...53 (2) and d < 4 μm (3) suspended through the vibrator during irradiation in the V = 5 ml water under the influence of γ-quanta (^{60}Co, P=19.5 rad/s, T = 300 K)), which are determined according to BeO, on its mass

If the amount of molecular hydrogen changes as:

$$\Delta N = N(H_2) - N_0(H_2), \qquad (1)$$

by the addition of BeO (1), then the formation rate of molecular hydrogen according to BeO can be defined on the basis of (2):

$$w_{BeO}(H_2) = \frac{\Delta N}{m_{BeO}t} = \frac{N(H_2) - N_0(H_2)}{m_{BeO}t} = \frac{m_{water}}{m_{BeO}} \frac{N(H_2) - N_0(H_2)}{m_{water}t} = \frac{m_{water}}{m_{BeO}} \left[\frac{N(H_2)}{m_{water}t} - \frac{N_0(H_2)}{m_{water}t} \right] = \frac{m_{water}}{m_{BeO}} \left[w_{water}(H_2) - w_0(H_2) \right]. \qquad (2)$$

Here m_{BeO} – is the mass of BeO added to water. The radiation-chemical yield of molecular hydrogen according to BeO has been calculated on the basis of rate defined based on expression (2).

It has been defined from the results that the formation rate and radiation-chemical yield of molecular hydrogen (which is obtained from radiation - heterogeneous transformation of water in the systems of BeO with $d < 4$, $d = 32…53$ and 75…106 μm particle size suspended through the vibrator during the irradiation by adding into $V = 5$ ml bi-distilled water) defined according to water increase directly proportional in the lower values of BeO mass (see Fig. 4), but in the higher values the inclination angle decrease. The formation rate and radiatio-chemical yield of molecular hydrogen defined according to BeO remain almost constant in the lower values of BeO mass, but there is a decrease in the higher values. In these systems the maximum radiation-chemical yield of molecular hydrogen defined according to water is 2.79, 2.29, 1.66 according to $d < 4$, $d = 32…53$, 75…106 μm particle size, but that defined according to BeO is 208; 111; 68.7 molecile/100 eV.

The dependence of the process of obtaining molecular hydrogen from the radiation-heterogeneous transformation of water in the BeO/H_2Osystem on the mass and particle size of BeO can be explained on the basis of existing mechanisms of radiation-heterogeneous processes. When γ-quanta (^{60}Co, $E_\gamma = 1.25$ MeV) pass through the BeO/H_2O system, Compton scattering occurs mainly in both phases compared to other processes due to the interaction with the atoms and molecules that make up the system (photoeffect, electron-positron pair formation, etc.). Depending on the scattering angle, the kinetic energies of Compton electrons vary in the range of 0…1.02 MeV. Compton electrons, which have high kinetic energies, and each new generation δ-electrons they create, gradually lose their kinetic energies in elastic and inelastic collisions in both phases and become thermal electrons.

The process of energy transfer at the beryllium oxide/water boundary and as a result the formation of molecular hydrogen can be explained as follows. Within the beryllium oxide particle, some of positive ions formed by ionizing radiation are localized in volume

and some on the surface through traps due to the migration. Positively charged BeO^+ local centers create the complex:

$$BeO^+ + H_2O \rightarrow [BeO\cdots H_2O]^+ \quad (3)$$

as a result of ion-dipole interaction at the BeO/H_2O boundary. Then that complex is recombined with the tunnel and thermal electrons and creates electron-excitation complex:

$$BeO\cdots H_2O]^+ + e^- \rightarrow [BeO\cdots H_2O]^*. \quad (4)$$

The electron-excitation energy generated in the complex and inside the solid particle is transmitted to the adsorbed water molecule, causes the dissociation of the water molecule, and as a result creates highly reactive intermediate H and OH products:

$$[BeO\cdots H_2O]^* \rightarrow BeO\cdots OH+H \quad (5)$$

as a result molecular hydrogen $(H+H\rightarrow H_2)$.

The fact that the radiation-chemical yield of molecular hydrogen in suspension systems is higher than in other systems can be explained by the electrons emitted from the surface of the solid by adding to the liquid. Thus, as a result of migration, some electrons formed inside the particle can be localized in volume and in surface defects, and some can be emitted from the particle surface into water. Due to the electrons emitted from the solid to the liquid phase, the concentration of electrons [17–19] is higher in the liquid phase around the solid particle particle than in other particles. The electrons emitted into the water gradually lose their kinetic energy as a result of the collision and are converted first into heat and then into solvated electrons. Molecular hydrogen is obtained from reactions (6–8) between solvated $\left(e_{aq}^-\right)$electrons and water molecules, protonated (H_3O^+) water molecule and H atoms.

$$2e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^-, \quad (6)$$

$$e_{aq}^- + H + H_2O \rightarrow H_2 + OH^-, \quad (7)$$

$$e_{aq}^- + H_3O^+ \rightarrow H_2 + H_2O. \quad (8)$$

So, if both the mass and particle size of BeO change, the energy carriers transferred to the water, as well as the corresponding radiation-chemical yield of molecular hydrogen, change. However, after a certain concentration of particles with each size in the environment, a balance is established between the processes of formation of energy carriers and intermediate products.

The following results have been obtained on the basis of the research:

- The amount, formation rate and radiation-chemical yields of molecular hydrogen defined according to water, obtained from radiation - heterogeneous transformation of water in the systems formed by V = 5 ml bi-distilled water and the addition of BeO with the mass of m (g)=0.01; 0.02; 0.04; 0.08; 0.2 and the particles size of d < 4, d = 32...53, 75...106 μm, suspended through the vibrator during the irradiation in the same amount water under the influence of γ-quanta (^{60}Co, P = 19.5 rad/s, T = 300 K), increase directly proportional in the low values of mass depending on the particle size of BeO, but there is a decrease in the inclination angle in the high values. In these systems, the maximum radiation-chemical yield of molecular hydrogen determined for water are – 2.79; 2.29; 1.66 molecules/100 eV according to the particle size;
- In these systems, the formation rate and radiation-chemical yield of molecular hydrogen determined for BeO remain almost constant at low values of mass depending on the particle size of BeO added to water, but there is observed a decrease at high values. Maximum radiation-chemical yields of molecular hydrogen determined according toBeO in the got the values of 208; 111; 68.7 molecule/100 eV

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ВЛИЯНИЕ МАССОВЫХ И РАЗМЕРНЫХ ЭФФЕКТОВ НА ПРОЦЕСС РАДИОЛИЗА ВОДЫ В СУСПЕНЗИРОВАННОЙ СИСТЕМЕ BeO/H_2O ПОД ВОЗДЕЙСТВИЕМ ГАММА-КВАНТОВ

Я.Д. Джафаров

В пересчете на воду и BeO были определены количество, скорость образования и радиационно-химический выход молекулярного водорода, полученного в результате радиолиза воды внутри пористых суспензированных систем BeO/H_2O под воздействием γ-квантов (^{60}Co, P = 19,5 рад/с, T = 300 К). При этом объем воды (V = 5 мл) поддерживался постоянным, а изменялись только масса (m_{BeO} = 0,0 (чистая вода), 0,01; 0,02; 0,04; 0,08; 0,2 г) и размер (d < 4, d = 32…53 и 75…106 мкм) частиц оксида бериллия. Было обнаружено, что в этих системах количество, скорость образования и радиационно-химический выход молекулярного водорода, определяемые как для воды, так и для BeO, варьируются в зависимости от массы и размера частиц BeO, добавляемых в воду.

ВПЛИВ МАСОВИХ І РОЗМІРНИХ ЕФЕКТІВ НА ПРОЦЕС РАДІОЛІЗУ ВОДИ В СУСПЕНЗОВАНІЙ СИСТЕМІ BeO/H_2O ПІД ВПЛИВОМ ГАММА-КВАНТІВ

Я.Д. Джафаров

У перерахунку на воду і BeO були визначені кількість, швидкість утворення і радіаційно-хімічний вихід молекулярного водню, отриманого в результаті радіолізу води всередині пористих суспензованих систем BeO/H_2O під впливом γ-квантів (^{60}Co, P = 19,5 рад/с, T = 300 К). При цьому обсяг води (V = 5 мл) підтримувався постійним, а змінювалися лише маса (m_{BeO} = 0,0 (чиста вода); 0,01; 0,02; 0,04; 0,08; 0,2 г) і розмір (d < 4, d = 32...53 і 75...106 мкм) частинок оксиду берилію. Було виявлено, що в цих системах кількість, швидкість утворення і радіаційно-хімічний вихід молекулярного водню, що визначаються як для води, так і для BeO, варіюються в залежності від маси та розміру частинок BeO, що додаються в воду.