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COMBINATION OF ELECTRO- AND RADIOCHEMICAL PROCESSES FOR HYDROGEN AND OXYGEN OBTAINING

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It is shown that increase in the hydrogen production process efficiency can be ensured by integrating radiochemical and electrochemical processes. In this case, the obtained effect depends not only on the direct radiolysis of water, but also on the involvement of the ionizing radiation energy in the electrolysis process for the excitation of water molecules that undergo electrolysis, which leads to a decrease in the consumption of electricity for the decomposition of its gaseous components. An analysis of the main factors influencing the reduction of electricity consumption during electrolysis is presented, and the affinity of the spectra of radical ions involved in the radiation and electrochemical processes of water decomposition is shown. As a result of radiation exposure, the most energy-intensive stage of water decomposition, associated with the breaking of intermolecular bonds and the formation of active particles involved in the electrochemical process, begins. It was established that the formation of hydrogen increases due to the addition of its direct output during radiolysis and indirect production during electrolysis, initiated by the activation effects caused by ionizing radiation. It is shown that in order to increase the direct radiolytic yield of hydrogen, elements containing nanosized zirconium dioxide powder should be placed in the interelectrode space of the electrolyzer. It has also been proven that the irradiation of zirconium dioxide placed in water leads to a 4-fold increase in the yield of hydrogen compared to the option of irradiating pure water. To increase the energy potential utilization coefficient of nuclear fuel at NPPs, it is expedient to use the energy of fuel elements located in spent nuclear fuel storage pools for the application of the proposed technology. This will ensure the utilization of the ionizing radiation energy, which in existing technologies is irretrievably lost, because it is discharged in the form of low-temperature thermal emissions into the environment, which leads to thermal pollution of the atmosphere.

***Keywords**: hydrogen, electrolysis, spent fuel elements, energy, water molecules.*

Introduction

Hydrogen obtaining by electrolysis of water is one of the most mastered technological processes in industry [1–4]. Its main drawback is the high energy and metal consumption of the equipment, which is caused by the low energy density on the electrodes due to the superficial nature of the electrolysis process. In view of this, the search for new ways of solving the problem of reducing electricity costs for hydrogen production and improving the design of electrolysis equipment is urgent. One of the possible ways to solve this problem is the superimposition of energy fields of different physical nature for the energetic excitation of water that decomposes in electrode processes. For example, there are known attempts to combine photolysis and electrolysis to obtain hydrogen [5]. The proposed material considers the fundamental possibility of using the ionizing radiation energy arising in nuclear reactions to activate electrochemical processes and improve their energy characteristics.

Theoretical aspects of the use of the ionizing radiation energy in water decomposition processes

The reason for the special interest in radiochemical methods is the possibility, importantly, of direct conversion of the energy of nuclear radiation into the energy stored in hydrogen. The efficiency coefficient of the water radiolysis process and aqueous solutions at a neutron flux density of up to 10^{13} $cm^{-2}\cdot s^{-1}$ does not

exceed 6%. However, the radiolysis process is of practical interest because it occurs at low temperatures and can be combined with other methods of hydrogen obtaining. An increase in the yield of molecular products of radiolysis is possible due to a decrease in the rate of recombination of radicals H^+ and OH^- and reverse reactions. Decrease in the speed of the latter is achieved thanks to the introduction of substances capable of redox reactions, such as iron salts, oxalic acid, etc., into the solution.

In the proposed option, this role will be played by electromagnetic phenomena induced in the interelectrode space by the difference in electric potentials during the electrolysis of water. It should be noted that the problem of effective production of commercial hydrogen using nuclear radiation is promising, yet poorly developed, since until recently the research of experts in the field of nuclear energy was aimed at solving the reverse task, namely, suppressing the release of hydrogen and oxygen in the water circuits of nuclear power and technological installations in order to prevent flooding of structural materials or the formation of a noisy mixture of hydrogen and oxygen.

A nuclear reactor is a source of heat and radiation [6]. Therefore, in addition to the use of heat for the generation of electricity or their technological application in the chemical and metallurgical industries, it is promising to use ionizing radiation to create a radiation-chemical technology for hydrogen obtaining.

This effect can be manifested only in the case when the ionizing radiation energy is used in a way, which is different from thermal (direct purpose), namely, obtaining highly reactive components for further transformation into products of water electrolysis. Slightly more than 6% of the thermal power of nuclear radiation can be used from radiation-chemical processes. However, taking into account the huge capacities of fuel elements, measured in thousands of megawatts, the amount of energy involved in the process of hydrogen obtaining will be sufficient to organize its large-scale production. In this regard, the use of nuclear energy as a source of radiation for hydrogen obtaining is considered as very promising for large-scale hydrogen production by some researchers [2, 4].

It is seen as appropriate to consider the issue of combining radiation and electrochemical processes, in which ionizing radiation will ensure the activation of water during electrolysis, reducing the cost of electrical energy for this process.

The main goal of this paper is to evaluate the fundamental possibility of using the energy of spent nuclear power plants to increase the efficiency of hydrogen generation by conducting electrochemical processes in combination with ionizing radiation, which will allow to consider the holding basins as an element of the atomic-hydrogen energy technological complex, which ensures a more complete use of the nuclear fuel potential.

Integration of radiochemical and electrochemical processes during water electrolysis

Increase in the efficiency of the hydrogen production process can be ensured by integrating radiochemical and electrochemical processes. In this case, the effect can be obtained not only in the direct radiolysis of water, but also from the involvement of the ionizing radiation energy in the electrolysis process to excite the water molecules that undergo electrolysis, which leads to a decrease in the consumption of electricity for the decomposition of their gaseous components by electrolysis. In electrolyzers, the exchange current at the electrodes is an important kinetic characteristic of the electrochemical reaction, which depends on the activity of the reacting ions and the activation energy of the electrode processes. From the point of view of large-scale production of hydrogen due to the use of atomic energy, the process of high-temperature electrolysis of water vapor with the simultaneous imposition of the physical effect of ionizing radiation on the process of decomposition of water molecules under the action of an electric current is more rational. In this case, a more complete use of the potential of nuclear fuel is ensured, since not only the thermal effect of irradiation is used, but also the radiation component of the nuclear fuel fission energy is involved in the technological process of hydrogen obtaining.

The material located in the zone of ionizing radiation absorbs the energy of three types of radiation: 1) fast neutrons generated during the distribution, which are slowed down and thermalized during collisions with the atoms of the present material; 2) γ-rays, which are mainly formed during distribution, and emitted by products of distribution; 3) β-rays, which can be formed due to radioactivity induced in the material itself, and from radioactive radiation that depends on the type of reactor and varies from point to point in the reactor volume.

Regardless of whether the initial radiation is penetrating electromagnetic waves (γ-rays) or charged particles (β-rays), in all types of radiation the agent that affects water is the same fast-moving electron. Usually, β- and γ-rays from radioactive substances have energies from 0.3 to 3 MeV. This potential is sufficient for the destruction of a water molecule [7].

Deviation in liquid water can be hydrogen-bonded and localized, leading to the formation of H, OH, H_2 and H_2O_2 [8]. There are two possible ways of formation of excited water molecules: 1) when the H_2O^+ ion captures the ejected electron (Samuel-Maga hypothesis); 2) due to collisions of slow electrons with water molecules, as a result of which water molecules can appear in non-equilibrium singlet and triplet states in a ratio of 1 to 3.

Irradiation leads to the decomposition of water into hydrogen and oxygen and the formation of hydrogen peroxide, as well as free radicals. The resulting molecular decomposition products are called stable. They are electroneutral, unlike short-lived free radicals. Although oxygen is among the products of decomposition, it is apparently not formed directly from water, but as a result of the action of radicals on hydrogen peroxide. All radiation that occurs in a nuclear reactor as a result of a nuclear reaction transfers its energy through fast charged particles that can be divided into light and heavy ones (electrons or atomic ions, respectively). As a result, molecular reaction products and a whole range of free radicals with high reactivity are formed. At the same time, molecular products are formed in a significantly smaller amount than free radicals, which simultaneously arise and initiate the process of water decomposition. The value of the ionization potential of water can be found from data on the ionization potentials of gaseous oxygen and hydrogen. It lies in the range of values from 66 to 69 eV [9].

To evaluate the effectiveness of chemical processes excited by radiation, the value of the radiation yield of hydrogen in the processes of water decomposition is used. The said value is the number of hydrogen molecules per 100 eV of absorbed energy [10].

Despite the fact that chemical reactions in irradiated solutions can be explained by independent ways of formation of radical and molecular products, in fact both types of products are the result of the same process, and the difference between heavy and light radiation is due to the different spatial arrangement of the radicals that arise. A fast electron transfers energy of about 100 eV to water. It is enough to decompose several water molecules with the formation of groups of free radicals located at a distance of 10–20 A° one from another. Free radicals arise as a result of a combination of physical and chemical processes initiated by the passage of an ionizing particle through water. The transfer of the ionizing radiation energy to water takes place in a very small amount of time (10^{-16}–10^{-18} s). At the same time, excited water molecules and ions H_2O^+ and secondary electrons arise. The latter have significant energy, which is sufficient to ionize and excite several water molecules [3, 11]. This prompts the following reactions to occur in the irradiated water, with the formation of free radicals, ions and molecular products.

$$H_2O + H_2O \rightarrow H_3O^+ + OH. \quad (1)$$

The electron is then attracted to the ion

$$H_3O^+ + e^- \rightarrow H_3O. \quad (2)$$

A particle of H_2O can undergo thermal dissociation in two ways:

$$H_3O \rightarrow H + H_2O; \quad (3)$$

$$H_3O \rightarrow e^-_{aq} + H_3O^+. \quad (4)$$

Formation of particles OH and H_3O occurs due to the ionization of one among the two water molecules connected by a hydrogen bond.

Thus, after the passage of an ionizing particle, there are radicals OH, e^-_{aq}, ions H_3O^+ and excited water molecules in the track. Their concentration is sufficiently high (~0.1–1.0 M), and therefore they interact with each other by means of diffusion

$$e^-_{aq} + OH \rightarrow OH^-; \quad (5)$$

$$e^-_{aq} + H_3O^+ \rightarrow H + H_2O; \quad (6)$$

$$e^-_{aq} + e^-_{aq} + H_2O \rightarrow H_2 + 2OH^-; \quad (7)$$

$$e^-_{aq} + H + H_2O \rightarrow H_2 + 2OH^-; \quad (8)$$

$$OH + OH \rightarrow H_2O_2; \quad (9)$$

$$H + H \rightarrow H_2; \quad (10)$$

$$H + OH \rightarrow H_2O; \quad (11)$$

$$H_3O^+ + OH^- \rightarrow 2\ H_2O. \quad (12)$$

The specified processes have high rate constants that lie in the range (5×10^9–10^{11} l/mol·$s^{27\text{-}52}$). Reactions (9)–(12) lead to the formation of so-called molecular products of water radiolysis (H_2 and H_2O_2), and reaction (8) leads to the formation of H atoms.

A comparative analysis of the spectra of ion-radicals formed in the process of ionizing radiation shows the similarity of their composition and the composition of radicals, which are involved in the electrolysis process and require the expenditure of electrical energy for their formation. Thus, in the proposed option, the radiation component ensures the activation of water due to the kinetic energy of the fission of radioactive material with the accumulation of active particles and their subsequent conversion due to energy exchange between themselves and with water molecules.

Ionizing radiation, which affects water, transfers its molecule to an energetically excited state due to the interaction of charged particles that maintain it in a thermodynamically unbalanced state. The presence of a radiation-activated part in the electrolysis zone leads to a change in the kinetic and energy characteristics of water decomposition processes [12]. It should be noted that the integral effect of all types of radiation characteristic of nuclear reactions is determined by the electronic component, which affects the degree of activation of electrolysis processes, and the role of electrochemical processes, unlike traditional electrolysis, is practically reduced to the electrochemical separation of the produced gases, which requires significantly lower electricity consumption. An additional factor affecting the energy intensity of the process can be the effect of the appearance of radiation defects on the surface of the electrodes, which increases their activity and reduces the polarization potential of the overvoltage at the phase interface, which depends on the energy intensity of electrolysis.

In order to increase the direct radiolytic yield of hydrogen in the interelectrode space of the electrolyzer, elements, which include nanosized zirconium dioxide powder, should be installed. Papers [13–16] show that the irradiation of zirconium dioxide or metal hydrides in water leads to a 4-fold increase in the yield of hydrogen compared to the option of irradiating pure water. The authors explain the experimentally established effect of radiation-chemical hydrogen release by intensive transfer of energy from the solid phase to water molecules. Due to the participation in this process of radiation-generated active centers on the surface, the latter are sources of secondary electron emission [17].

When using an electrolysis system operating on the principle of time-separated hydrogen and oxygen generation processes [18–20], in complex electro- and radiochemical technology, a significant (up to 80%) reduction in the electrical energy consumption for stimulating the oxidation process of the iron electrode should be expected (Fig. 1). This will reduce the energy consumption of the water decomposition process by 24% and provide an electrical energy saving of 1 kWh per production of 1 m^3 of hydrogen and 0.5 m^3 of oxygen.

Due to the strict norms for the operation of nuclear reactors, it is surely not allowed to interfere with the design of the elements of the first circuit. Therefore, as a source of ionizing radiation, it is proposed to use the spent fuel elements of exposure located in the pool,

Fig. 1. Design of an electrolysis cell

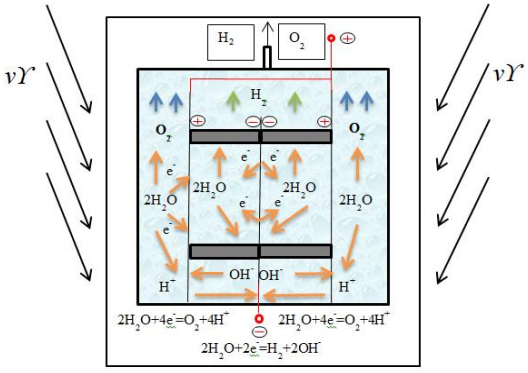

Fig. 2. Scheme of an electrolysis cell under the influence of ionizing radiation

access to which seems to be more realistic from a technical point of view, for the placement of electrochemical cells. The use of such a complex technology, which combines radiation and electrochemical processes within the framework of one unit (Fig. 2), makes it possible to ensure the generation of hydrogen with minimal consumption of the electrical component, which actually determines the cost of the produced hydrogen.

Ways of energy utilization of spent fuel elements in energy technology systems

In order to increase the utilization coefficient of the nuclear fuel energy potential, it is expedient to implement the proposed technology to use the energy of fuel elements in spent nuclear fuel storage pools, which will ensure the utilization of the ionizing radiation energy, which is irretrievably lost in existing technologies, as it is discharged in the form of low-temperature thermal emissions into the environment, which causes atmospheric pollution [21].

According to the operating regulations, the reactors at the NPP are periodically stopped for overloading to replace spent nuclear fuel and restore the reactivity reserve. The standard frequency of overloads is from one year to one and a half years. In case of overloading, part of the heat-emitting assemblies (from one third to a quarter) are removed to the storage pool, and fresh assemblies are placed in the active zone of the reactor. Annually, 25–40 tons of spent fuel are discharged from the high-capacity power reactor, which still has high radioactivity and is a source of intense radiation, which can be used to irradiate water in order to activate it and increase the efficiency of electrolysis processes for hydrogen obtaining.

The spent fuel storage system is designed to remove activity and residual heat emissions from spent heat-emitting assemblies to acceptable values for its transportation. To ensure reliable removal of residual heat emissions from used heat-emitting assemblies and to protect service personnel from exposure, the storage pool is filled with an aqueous solution of boric acid. This excludes the possibility of an involuntary chain reaction. In addition, this effect is enhanced due to the special design of the storage pool rack, in which the heat-releasing assemblies are installed in steps of 400. The water in each compartment of the storage pool circulates through the cooling system of the storage pool, which ensures an acceptable water temperature of no more than 70 ºC. In addition, the system cooling requires the presence of a protective water level of 3 to 4 m above the placed fuel elements (Fig. 3).

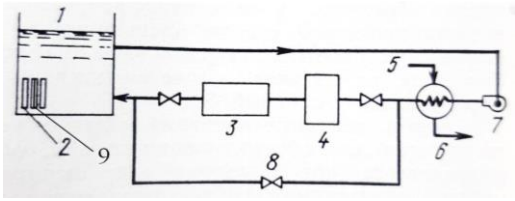

Fig. 3. Diagram of the spent fuel cooling system:
1 – spent fuel storage pool; 2 – spent fuel elements; 3 – desalination plant; 4 – filter; 5 – cooled water; 6 – heat exchanger; 7 – fuel storage pool pump; 8 – bypass; 9 – electrochemical cell

The capacity of the storage pool is approximately 400 pcs. assemblies. It ensures the durability of spent heat-dissipating assemblies for at least three years. After that, they are transported to the site of dry storage of spent nuclear fuel.

The economic expediency of investing in the further progress and practical development of the proposed method is determined by two factors: a drastic reduction in electricity consumption during the production of hydrogen and the expansion of the energy base for its industrial production due to the utilization of residual energy of nuclear fuel at nuclear power plants. Both of these factors are decisive for the organization of large-scale hydrogen production in Ukraine and the formation of the energy technological infrastructure of hydrogen energy.

Conclusions

1. An option of the combined use of electro-radiochemical methods of hydrogen obtaining is considered. As a result of this, it is possible to assume with high probability a decrease in electric energy for its production due to an increase in the electrical conductivity of the electrolyte, as well as the appearance of radiation defects on the surface of the electrodes, which ensure a decrease in polarization potentials on the surface of the phase separation. It is shown that when using an electrolysis system operating on the principle of time-separated hydrogen and oxygen generation processes in complex electro- and radiochemical technology, a significant (up to 80%) reduction in electrical energy consumption for stimulating the iron electrode oxidation process should be expected. This will reduce the energy consumption of the water decomposition process by 24% and provide an electrical energy saving of 1 kWh per production of 1 m^3 of hydrogen and 0.5 m^3 of oxygen.

2. The analysis of the main factors affecting the reduction of electricity consumption during electrolysis is presented, and the affinity of the spectra of radical ions participating in the radiation and electrochemical processes of water decomposition is shown. As a result of radiation exposure, the most energy-intensive stage of water decomposition occurs, associated with the breaking of molecular bonds and the formation of active particles that are involved in the electrochemical process, in which the electrolyzer performs the role of a gas product separator.

3. An increase in the formation of hydrogen due to the addition of its direct output during radiolysis and indirect production during electrolysis, initiated by the activation effects caused by ionizing radiation, was established.

4. The proposed solution provides an increase in the level of use of the reaction potential of nuclear fuel due to the utilization of the energy of spent fuel to obtain hydrogen and oxygen.

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Показано, що підвищення ефективності процесу одержання водню може бути забезпечене шляхом інтеграції радіохімічних та електрохімічних процесів. У цьому випадку отримуваний ефект залежить не тільки від прямого радіолізу води, а й від залучення в процес електролізу енергії іонізуючого випромінювання для збудження молекул води, які піддаються електролізу, що призводить до зниження споживання електроенергії для розкладання її газових компонентів. Наведено аналіз основних факторів, що впливають на зниження електроспоживання при електролізі, і показано спорідненість спектрів радикал-іонів, що беруть участь у радіаційних та електрохімічних процесах розкладання води. У результаті радіаційного впливу починається найбільш енергоємна стадія розкладання води, пов'язана з розривом міжмолекулярних зв'язків та утворенням активних частинок, що залучаються до електрохімічного процесу. Встановлено, що утворення водню збільшується завдяки додаванню його прямого виходу при радіолізі й опосередкованого одержання при електролізі, ініційованому активаційними ефектами, зумовлених іонізованим випромінюванням. Показано, що для підвищення прямого радіолітичного виходу водню в міжелектродному просторі електролізера слід розмістити елементи, які містять нанорозмірний порошок діоксиду цирконію. Доведено також, що опромінення діоксиду цирконію, поміщеного у воду, призводить до збільшення в 4 рази виходу водню в порівнянні з варіантом опромінення чистої води. Для підвищення коефіцієнта використання енергетичного потенціалу ядерного палива на АЕС доцільно для застосування запропонованої технології використовувати енергію ТВЕлів, що розміщуються в басейнах витримки відпрацьованого ядерного палива. Це забезпечить утилізацію енергії іонізуючого випромінювання, яке в існуючих технологіях безповоротно втрачається, тому що відводиться у вигляді низькотемпературних теплових викидів у навколишнє середовище, що призводить до теплового забруднення атмосфери.

Ключові слова: *водень, електроліз, відпрацьовані ТВЕли, енергія, молекули води.*

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