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HYDROGEN PRODUCTION, STORAGE, AND USE AT NUCLEAR POWER PLANTS

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The present status of the problems of safe storage and use of hydrogen in the world hydrogen-energy sector are analyzed. Specific examples of foreign and domestic designs of atomic-commercial complexes based on operating nuclear power plants, viewed as hydrogen producers and users, are presented. A method of producing hydrogen accumulators with cartridges which contain microcapsules or capillaries, made of high-strength materials and filled with hydrogen under high presure (above 100 MPa), is proposed as a promising direction for solving storage and use problems. The mechanisms of introducing/extracting hydrogen into/from microelements in the space of the accumulators up to a working pressure of 0.2–1 MPa are based on diffusion and active thermomechanical principles.

The nuclear and chemical industries, automobile manufacturing industry, the aerospace complex, all forms of transportation (automobile, marine, and railroad), manufacturing of portable sources of power (mobile telephones, computers, everyday technology), and other industrial sectors are all showing great interest in high-quality and rapid development of hydrogen as a source of energy.

Hydrogen power faces three basic problems: obtaining hydrogen by decomposition of water – electrolysis or thermolysis – or by the dissociation of hydrocarbons. The basic problems are to decrease the cost and direct conversion of the oxidation energy of hydrogen into electricity. This problem has already been solved technologically in our country and abroad with the assistance of various types of fuel cells, but the questions of their cost and service life, safe storage, and delivery to the consumer remain.

Two basic directions of hydrogen production are being examined in the nuclear power industry: the development of atomic-commercial complexes based on high-temperature gas-cooled reactors and using the energy generated at nuclear power plants during a period of low demand.

The design developed by the Russian Science Center Kurchatov Institute, the Leningrad nuclear power plant, and the Canadian companies AECL and Stuart Energy in 1990–1992 supposes that initially hydrogen is produced by electrolysis of water with power 30 MW, i.e., 14.5 tons/day. At the second stage of the design, the power of the electrolysis plant is to be increased to 300 MW. Electricity produced during a dip in the load on a nuclear power plant is to be used. At the Leningrad nuclear power plant, the underproduction during this period of time is approximately $400 \cdot 10^6$ kW·h/yr, which makes it possible to produce about 8000 tons hydrogen/yr. The hydrogen obtained is to be used for public transportation in Sosnovyi Bor and the excess hydrogen is to be sold to Finland. Another variant considered for utilizing the hydrogen obtained is to deliver it to the Kirishi petroleum processing plant. The oxygen obtained in so doing could become the basis for the production of ozone for purifying the industrial discharges in St. Petersburg [1]. Nuclear power plants can not only produce hydrogen; they are also hydrogen consumers. One of the main used for hydrogen at a nuclear power plant is for producing and supporting an optimal hydrogen water-chemistry regime in the coolant used in the reactor. In VVÉR pressurized-water reactors

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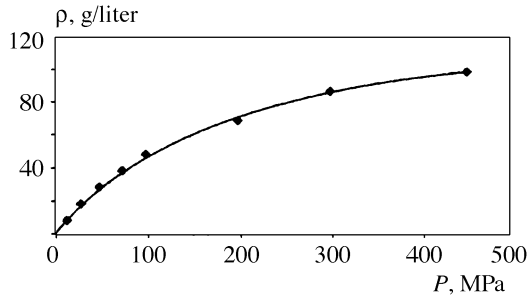

Fig. 1 Density of hydrogen gas versus pressure [5].

and, to a large extent, BWR boiling water reactors, hydrogen is introduced into the coolant to suppress radiolysis of the coolant and increase the service life of the fuel elements and the structural materials used in the components of the core and coolant circulation loops.

A substantial body of work was been done to search for and determine the optimal methods of dispensing hydrogen at nuclear power plants with RBMK reactors [2]. Experimental fuel assemblies for RBMK and AST reactors with volume boiling of water with steam content up to 3 mass% have been tested at the Russian Science Center Kurchatov Institute in MR loop setups. The setups were equipped with specially developed electrolyzers, built into the first loop (pressure up to 2 MPa), for working out a technology for maintaining the hydrogen regime of the coolant to suppress the radiolysis of water. One experimental fuel assembly for AST was tested under natural reactor conditions for 10 yr (more than 80000 h). Post-reactor investigations confirmed that this assembly is reliable and operable; dense protective oxide films ~5 μm thick formed on fuel-element cladding made of the zirconium alloy N-1. All fuel elements remained sealed.

In the USA, company owners must follow the NRC recommendations in using a specific method for producing, storing, delivering, and dispensing hydrogen in a way that meets the requirement for safety, siting, and operating hydrogen facilities, whose use depends on the operating conditions of a specific reactor. Nevertheless, as shown in [3], which is devoted to examining these questions, one of the main technical systems for dispensing hydrogen at nuclear power plants with BWR reactors is a cryogenic system using liquid hydrogen.

It should be noted that the systems for storing liquid and gaseous hydrogen, which must be placed outside the plant, must satisfy stringent requirements for fire and explosion safety and protection against external actions, such as, earthquakes, tornados, aircraft crashes, and terrorist acts.

Another important factor is the high capital investment required for such systems, estimated to be $3 \cdot 10^6$ dollars per unit with a typical BWR reactor neglecting operational expenses. Nonetheless, such high expenses are considered to be justified because the cost of repairing the equipment and pipelines of the circulation loop is lower because the corrosion of the structural materials is reduced.

Production requires developing systems for accumulating hydrogen. Their parameters with respect to the specific density must not be lower than those of liquid-hydrogen systems. They must provide maximum safety and be convenient to transport. American specialists consider this problem the main scientific challenge of hydrogen power. It is no accident that in the USA more than one billion dollars will be spent in 2003–2010 on solving these problems. The European Union plans to allot 2.8 billion euros to this problem. In our country, the integrated mining-metallurgical plant Noril'skii nikel' is giving the Russian Academy of Sciences up to 1 billion rubles per year to solve the problems of hydrogen power [4].

The existing methods for accumulating hydrogen (gaseous hydrogen under pressure in tanks) permit accumulating a small amount of hydrogen, there are restrictions on increasing this amount, and they also have low explosion safety characteristics. Hydrogen can be stored in a liquid form when cooled to –253°C (up to 7.1% of the mass content with respect to the mass of the storage site), but about one-third of the energy contained in the hydrogen (11 kW·h/kg) must be expended to cool the hydrogen to this temperature. The hydrogen losses to evaporation reach 3–5%/day. All other methods of accumulation using intermetallides, fullerenes, and adsorption on activated carbons allow a hydrogen content no higher than

TABLE 1. Requirements of the US Department of Energy for the Parameters of Hydrogen Carriers (accumulators)

Parameter	2007	2010	2015
Hydrogen mass relative to the mass of the carrier material, kg/kg	0.045	0.06	0.09
Hydrogen mass relative to the carrier volume, kg/liter	0.036	0.045	0.081
Time to reach the total hydrogen flow at 20°C, sec	4	4	0.5
Accumulator fill time, min	10	3	2.5

4.5 mass%. It has been concluded on the basis of an analysis of the existing methods for accumulating hydrogen that of all existing forms of the technology which has been realized and is ready to be adopted the highest mass content of hydrogen is reached in accumulators with gaseous hydrogen under pressure. The density of hydrogen under pressure above 200 MPa at temperature 291 K is higher than the density (70 g/liter) of liquid hydrogen at 20.4 K and 0.1 MPa (Fig. 1 [5]).

Accumulators must provide not only a high specific density of the hydrogen contained in them but it must be possible to fill them quickly and to extract the hydrogen at a rate which allows users to work efficiently, for example, an electrochemical generator.

The problem of loading and extracting hydrogen is solved operationally by using accumulators of gaseous hydrogen under pressure. But the tanks used for such accumulators have substantial limits on the hydrogen density and they are not highly reliable from the standpoint of explosion safety. In some countries limits are placed on the pressure of the hydrogen in tanks. As seen in Fig. 1, even the tanks which are now being developed with working pressure up to 70 MPa will contain hydrogen with density no higher than 40 g/liter.

The highest hydrogen density can be achieved in microporous structures based on microspheres or capillaries made of high-strength materials but the time required to fill such structures and extract the hydrogen – the diffusion mechanism [5] – from them does not meet the current requirements of the US Department of Energy, presented in Table 1. Consequently, to develop accumulators with a high hydrogen density the advantages of the methods of storing hydrogen in tanks – efficient extraction and prolonged residence in microporous structures under ultrahigh pressure – must be combined [6].

Figures 2 and 3 show microspheres and capillaries (the photograph was obtained using a high-resolution optical microscope). Materials which have high strength characteristics and low density – composite carbons and polymer materials – are of interest for developing a porous microstructure. Thus, the density of polymers fabricated on the basis of poly-p-phenyleneterephtalamide and other similar polymers of the aromatic series of aramides (armos, SVM, terlon, kevlar) is 5.5 times lower than that of steel and the strength characteristics are 5.6–10 times higher. For different brands of structural chromium–nickel steel the maximum strength can reach $\sigma_r \sim 550$ MPa. For aramides the tensile strength is 5500 MPa, and according to the data in [5] the maximum strength of quartz exceeds 7000 MPa.

The main characteristics of microporous structures from the standpoint of the effectiveness of storing hydrogen are the ratio of the maximum strength of the material of the shell of the microcapsules (microspheres, capillaries) to its density σ_r/ρ and the ratio of the thickness of the shell of the microcapsules to their radius δ/R (aspect number). Thus, the strength of armos is 10 times greater than that of chromium–nickel steel, and armos is more than 5 times lighter and the ratio of the maximum strength to its density is 49.4 times higher than for chromium–nickel steel.

The stress level arising in the shells of the microcapsules in a microporous structure under a pressure difference between inside and outside of the tank – the pressure in the tank – depends on the aspect number [7, 8]. Table 2 shows the dependence of the stresses σ_{eq} (stress intensity in a triaxial stress state in the structure) in the shell of the capillaries on the aspect number.

We shall now examine a variant of the structural solution for such accumulators. Carbon-plastic, quartz glass, multilayered materials, and high-strength polymer (for example, armos) can be used for the tank vessel and the shells of the microspheres or capillaries of a microporous structure. The accumulator consists of a shell–tank filled with a matrix consisting of a microporous structure [6]. The spheres are secured to one another by means of current-conducting materials based

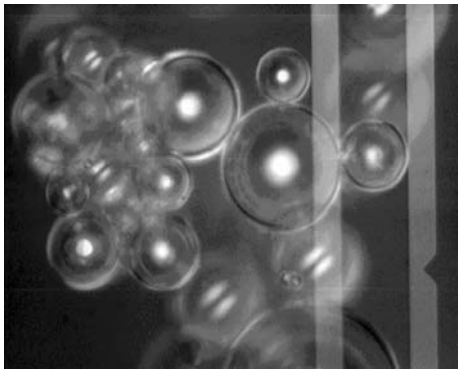

Fig. 2. Microspheres with diameter 30 μm.

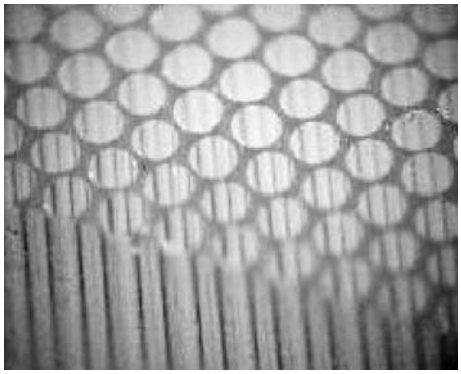

Fig. 3. Matrix consisting of capillaries.

on metal, graphite, or current-conducting glue. This permits heating the microporous structure, in order to increase the rate at which hydrogen is extracted from it, by passing a current along such a material. Such an accumulator makes it possible to feed hydrogen, at any time, from the space between the microspheres or capillaries to fuel cells, and by heating the microporous structure permeate the the space between the microspheres with hydrogen. In such a structure, the rate of hydrogen extraction from the microporous structure is no longer so critical, since a large buffer system containing hydrogen is created.

The results of calculations of the hydrogen content in accumulators with different hydrogen pressure in the microspheres and the space between the spheres are presented in Table 3. The characteristics of the accumulator are as follows: tank diameter 50 mm, tank length 1000 mm, aspect number 0.05, interior volume 1.66 liters, density of the material of the tank and armos microspheres 1.45 g/cm^3, and mass of a tank with a matrix consisting of a microporous structure 714 g. As Table 3 shows, even with 10 MPa hydrogen pressure in the tank the characteristics of the accumulator are no worse than those of the US Department of Energy for 2010 (see Table 1). The computational results (Table 2) show that a high hydrogen content is attained in the capillary cartridges.

About half of the world production of oil is consumed for transportation. It is this industry that is actively adopting the use of hydrogen as a fuel, which, aside from everything else, is capable, first and foremost, of solving the ecological problems of large cities and industrial regions. Such accumulators–cartridges can be installed, for example, in 200×200 mm and 1000 mm long containers with 16 cartridges in each container. Three containers hold from 4.3 to 6.35 kg of hydrogen, including 144 g at 10 MPa, 489 g at 35 MPa, 978 g at 100 MPa in the space between the spheres. When the valve is opened, this hydrogen can be fed to the user immediately. As the hydrogen is consumed, it is replenished from the matrix of the microporous structure. Figure 4 shows the basic structure of a hydrogen accumulator [6].

TABLE 2. Hydrogen Content in an Accumulator with Capillaries Made of Polymers ($\rho = 1.45$ g/cm^3) and Glass ($\rho = 2.5$ g/cm^3) under Pressure 100 MPa

Aspect number δ/R	Stress in a capillary, σ_{eq}^{max}, MPa	H_2 mass relative to the capillary (polymer) mass, %	H_2 mass relative to the capillary (glass) mass, %	H_2 mass relative to the capillary volume, kg/liter
0.01	8704	169.3	98.2	0.049
0.02	4418	83.6	48.5	0.048
0.04	2210	40.5	23.5	0.046
0.05	1776	31.9	18.5	0.045

TABLE 3. Characteristics of a Hydrogen Accumulator with a Matrix of Microspheres

Tank		Microspheres		Total hydrogen mass, g	Ratio to tank mass, %	H_2 mass relative to the tank volume, kg/liter
P, MPa	σ_{eq}, MPa	*P*, MPa	σ_{eq}, MPa			
10	178	300	2760	98.3	13.8	0.0492
35	622	200	1570	89.7	12.6	0.0448
35	622	300	2522	15.5	14.8	0.0528
35	622	450	3950	116.2	16.3	0.0581
100	1776	200	79.4	99.8	14	0.05

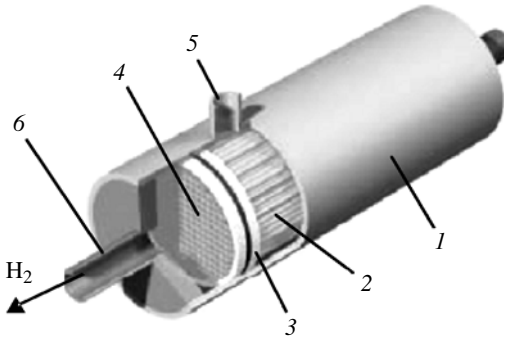

Fig. 4. Basic construction of a hydrogen accumulator: *1*) tank vessel; *2*) capillaries with hydrogen; *3*) heater; *4*) collector for feeding–extracting hydrogen; *5*) nipple for attaching a protective valve; *6*) nipple for releasing hydrogen.

Microporous stuctures make it possible to develop hydrogen accumulators with the most diverse structures and any sizes from hydrogen accumulators for portable sources of supply (mobile telephone, computers, everyday technology) to hydrogen accumulators for transportation and the aerospace complex. Such accumulators are safe, which is shown in the result of experimental studies [5] of superstrong microtanks – accidental destruction of one microtank does not result in any damage to the other tanks.

The development of technical systems for producing and accumulating hydrogen will produce multilevel ecologically clean technological complexes based on nuclear power plants. In the future, hydrogen accumulators based on microporous structures will supply users of hydrogen not only in the region of a nuclear power plant but also in regions far from a

plant where an infrastructure already exists. The high density of hydrogen, the absence of losses, which are inherent to, for example, the cryogenic variant of storage and transport, and the high explosion and fire safety will create good prerequisites for developing this direction.

The material presented in this paper is based on the results of theoretical and experimental studies of the properties of superstrong microtanks for hydrogen, performed at the P. N. Lebedev Physics Institute [5] since 1974, for developing laser targets for spherical compression and heating of plasma. The problems of working out a nanotechnology for fabricating microspheres from various materials are reflected in this work, hydrogen diffusion in the experimental materials was studied, and direct experiments to determine the maximum hydrogen pressure in microspheres made of the high-strength materials were performed.

The present paper proposes two fundamental variants of hydrogen accumulators with high parameters based on the use of microporous structures with microspheres and capillaries for practical implementation in research work [5]. Organizational-practical measures for working out a nanotechnology for fabricating capillaries from glass, quartz, and various polymers based on the high-precision technology of glass fiber and x-ray optics are now being taken. The problems of computational-experimental validation of the strength and reliability of the structural components of accumulators where the materials used for the microcapsules are exposed to corrosive media, protection against corrosion (nanotechnology for depositing protective coatings), hydrogen embrittlement of materials, cyclic damage, methods for rapidly filling accumulators with hydrogen up to a high pressure, delivering the product to the user, and others are being solved.

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