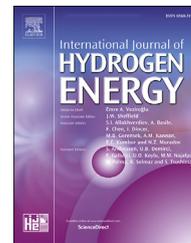


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# Magnesium hydride based hydrogen chemical source: Development and application perspectives

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## HIGHLIGHTS

- The process of hydrolysis of magnesium hydride with water vapor was studied.
- The peculiarities of the hydrolysis of magnesium hydride powder with water vapor were stated.
- The possibility of creating a chemical source of hydrogen based on this process was considered.

## ARTICLE INFO

### Article history:

Received 4 July 2019

Received in revised form

23 August 2019

Accepted 12 September 2019

Available online 13 October 2019

### Keywords:

Hydrogen source

Magnesium

Magnesium hydride

Hydrolysis

Water vapor

## ABSTRACT

In this paper, we studied the process of hydrolysis of magnesium hydride with water vapor and considered the possibility of creating a chemical source of hydrogen based on this process. To study the hydrolysis reaction of magnesium hydride powder at temperatures above 100 °C, an experimental setup with a quartz tube — a reactor 300 mm long — was designed. The mass and volume of a single powder load in a quartz reactor was 65 g and  $130 \pm 2 \text{ cm}^3$ , respectively. The length of the powder zone along the axis of the reactor was approximately 10 cm.

Based on the data obtained during the experiment, it can be distinguished that the length of the reaction zone is greatest at the beginning and at the end of the hydrolysis process and is approximately 5–6 cm. In the middle of the hydrolysis process, for the time interval from 3000 to 5000 s, the reaction zone is the smallest - about 4–5 cm. The proposed design of the hydrolysis reactor and the experimental setup also made it possible to study the peculiarities of the hydrolysis of magnesium hydride powder with water vapor; magnesium, the composition of the reaction products and the controllability of the generation of a stream of hydrogen.

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## Introduction

In recent years, the market of mobile electronic devices and unmanned autonomous systems has been actively

developing. Often the capabilities of these extremely useful gadgets and technical systems are limited by the capacity and power of the on-board power sources, which are most often types of batteries. Under these conditions, more and more

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<https://doi.org/10.1016/j.ijhydene.2019.09.094>

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attention is paid to hydrogen fuel cells (FCs) as a practical alternative to batteries.

The most important parameter for the on-board energy source is the specific energy intensity, which characterizes the ratio of the energy reserve ( $W \cdot h$ ) to the mass of the source (kg). Modern lithium rechargeable batteries are characterized by a specific energy capacity of 200  $W \cdot h/kg$ . For a multiple increase in the specific energy reserve, hydrogen fuel cells are of interest, due to the combination of high energy intensity of hydrogen 33  $MJ/kg$  and high efficiency of fuel cells  $>50\%$ . Hydrogen has the highest energy intensity (33.3  $kW \cdot h/kg$ ) among all other types of natural fuels. Comparison of energy intensity of the systems on fuel cells with traditional energy storage devices is given in Table 1 [1].

Today, hydrogen fuel cells are increasingly used in various areas of technology: primary energy sources, backup energy sources, autonomous power systems, electrical power plants for motor vehicles, portable energy sources. Despite all the advantages of hydrogen fuel cells, to achieve high specific characteristics of an on-board or portable power source in terms of energy consumption, it is necessary to ensure a high hydrogen storage density. Hydrogen is the lightest gas and, accordingly, achieving its high storage density is associated with great technical difficulties. The use of liquid, compressed and chemically bound hydrogen is the opportunity provided by the current level of technology.

The most widely used are technologies of hydrogen compressed in high-pressure vessels. This approach - hydrogen compressed to 300 or 700 bar and lightweight PEMFC, provide a sufficiently high specific energy capacity at the level of 500–600  $W \cdot h/kg$ . Nevertheless, despite all the advantages of this tandem, it has a significant drawback - the need to use equipment and pressure vessels, which entails the potential danger of depressurization and explosion. It is obvious that the use of such equipment and autonomous devices having on-board systems with high hydrogen pressure should be strictly regulated and limited in places with high population density. These restrictions stimulate the development of chemical sources of hydrogen, which can potentially provide a high density of hydrogen storage and the safety of technical systems based on them.

Reversible hydrogen storage in the form of metal hydrides of AB, AB<sub>2</sub> and AB<sub>3</sub> types is a safe and compact method (bulk density 120  $g/l$ ), however, it is characterized by low mass density ( $<2 \text{ wt}\% \text{ H}_2$ ). Therefore, metal hydride energy storage devices are suitable for stationary systems for which the weight of the energy storage device does not play a critical role; they are of little use for mobile energy sources because of the low specific characteristics of capacity or because of the

complexity and weight of the accompanying temperature-controlled equipment.

Storage of hydrogen in the form of magnesium hydride allows to increase the mass density of storage to 7.2%. Recent advances in research to improve the kinetic characteristics of the hydrogenation process are exhaustively presented in a recent review [2].

Chemical sources of hydrogen are based on several classes of chemical compounds: alanates, hydrides of alkali and alkaline earth metals, and borohydrides [3]. One of the most frequently used and applied in practice is sodium borohydride, which has gained its popularity due to its availability, relatively low cost, rather high characteristics of the specific energy storage density per unit mass or volume [4–6]. There are publications and patents in which the process of catalytic hydrolysis of sodium borohydride is investigated and energy systems based on this process of hydrogen generation are described [7–13]. However, the system has disadvantages, among which is the need to use a catalyst for the hydrolysis of sodium borohydride solution and the limited water solubility of the hydride itself and the reaction product. These shortcomings lead to the deposition of the reaction product on the surface of the catalyst and its degradation, which reduces the kinetics of hydrogen generation. Another known way is to obtain hydrogen by hydrolysis of inexpensive and readily available metal powders (Al, Mg) [14–17]. However, the mass fraction of generated hydrogen is only 2.5 and 3.3% during the hydrolysis of aluminum and magnesium, respectively. To increase the mass capacity of the source of hydrogen, it is possible to use metal hydrides or alloys [18–20]. So, during hydrolysis of magnesium hydride, the mass fraction of generated hydrogen is 6.4%, therefore, hydrogen generation by hydrolysis of  $MgH_2$  is a promising method for mobile and portable applications [21,22]. In this paper, the authors chose magnesium hydride as the base raw material for developing a prototype mobile power source with high specific energy storage characteristics. Magnesium hydride powders are obtained by the authors according to the original hydrogenation technology developed earlier.

To date, there are several works where a method of hydrolysis of magnesium hydride powders in a liquid medium is being developed. This method is complicated by the fact that in the process of hydrolysis on the surface of particles of magnesium hydride powder forms a hardly soluble passivating layer of magnesium hydroxide, which greatly reduces the yield of hydrogen in the course of the reaction. However, this problem is solved by the fact that excipients that change the pH of the solution and destroy the hydroxide layer are introduced into the solution. As such substances, various

**Table 1 – Energy storage and conversion systems.**

Energy storage/conversion unit	Specific capacity, $W \cdot h/kg$	Volume capacity, $W \cdot h/l$	Efficiency, %	Daily losses, %
Pb batteries	30–50	50–80	70–92	0.1–0.3
Ni/Cd batteries	50–75	60–150	60–70	0.2–0.6
Li-ion batteries	75–250	200–600	85–90	0.1–0.3
Na/S batteries	150–240	150–240	75–90	20
Supercapacitors	$<30$	100000	97	5–40
Hydrogen + FC	170–1500	500–3000	50–70	No

groups of developers use metal salts [12], organic acids [19,23]. This approach allows us to develop a fairly reliable and well-controlled system that ensures the generation of a stream of hydrogen within specified limits by dispensing briquettes or paste-like substances containing magnesium hydride particles in a liquid medium. Despite all the advantages of this approach, its use does not allow to achieve high performance in specific energy intensity, only because carrying out the hydrolysis reaction according to this scheme, in addition to the requirement for the introduction of auxiliary substances, should ensure that there is always a significant excess of liquid.

Alternatively, another approach to the hydrolysis process can be considered, while simultaneously removing both of the above drawbacks - high-temperature steam hydrolysis. When carrying out the hydrolysis process at temperatures significantly higher than 100 °C, the passivating magnesium hydroxide layer on the surface of the magnesium hydride particles becomes “loose” and does not represent an obstacle to the penetration of the vapor-gas mixture. The need for the reaction of high-temperature hydrolysis with an excess of water vapor is also eliminated, since at high temperatures the powder activity is quite high and the hydrolysis reaction should proceed almost completely. An analysis of the publications showed that such development was carried out in particular at the NASA Jet Propulsion Laboratory [24], but no further reports of the completion and use of this device followed.

This publication presents the results of the first stage of work aimed at developing a power source with a chemical hydrogen source based on hydrolysis of magnesium hydride with water vapor. The main requirements for a chemical source of hydrogen are to provide a stable and well-controlled flow of hydrogen in a certain range of environmental conditions, to ensure the full use of reagents. The chemical source of hydrogen in question is a heterogeneous chemical reactor. The physicochemical processes occurring in this type of reactor are generally well known and can be described in the form of a mathematical model with a set of differential equations describing the processes of heat-mass transfer and chemical interactions. However, due to the small scale of such a reactor and the large number of mutually affecting parameters, it is not possible to build a model that can reliably predict the behavior of such a system in the range of operating conditions and environmental conditions of interest. Moreover, experimental studies of such systems show their extremely unstable behavior, and demonstrate difficulties in constructing control algorithms. Thus, there is a need to build a model stand - a prototype of a chemical source of hydrogen on the hydrolysis of magnesium hydride, to study the basic laws of the process of hydrolysis in the interesting range of environmental conditions and the scale of the system.

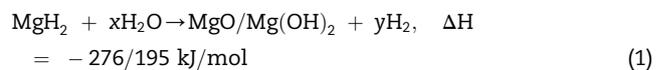
## Experimental details

We used magnesium hydride powder obtained in-house in the hydrogenation reactor and according to our own development process [25]. Magnesium powder MPF-4 was used to synthesize magnesium hydride. The chemical composition of the powder of the original magnesium prior to the process of hydrogenation: active magnesium is not less than 99 wt%, Fe < 0.05 wt%, Cl < 0.005 wt%. The content of magnesium hydride in the hydrated powder was estimated by two independent methods: by weight gain and by volume of hydrogen emitted during hydrolysis of the powder in an acid solution and was not less than 95 wt%. The granulometric composition of the powder of magnesium hydride was determined in a laser granulometer Fritsch Analysette 22 (Table 2):

When studying the hydride hydrolysis reaction, a quartz cylinder with an inner diameter of 43 mm and a wall thickness of 5 mm was used as the reactor vessel. The cylinder length was 300 mm. On both sides of the quartz cylinder flanges with silicone rubber seals were located. The flanges were tightened with four steel studs and had inlets for water and a hydrogen outlet. On the water inlet side, the flange had an additional sealed inlet for the thermocouple in a stainless steel case. The thermocouple touched the metal stop limiter, which was used to fix the magnesium hydride powder inside the quartz cylinder. Outside the quartz tube resistive wire heater was located, which was used for the initial heating of the metal stop-limiter and part of the magnesium hydride powder. In addition, a cylindrical heat insulator made of a 10-mm-thick layer of aluminosilicate fiber was placed on the quartz tube, which could move along the axis of the quartz tube. The experimental setup for studying the hydrolysis reaction is shown in Fig. 1.

The mass and volume of a single powder load in a quartz reactor was 65 g and  $130 \pm 2 \text{ cm}^3$ , respectively. The length of the powder zone along the axis of the reactor was approximately 10 cm.

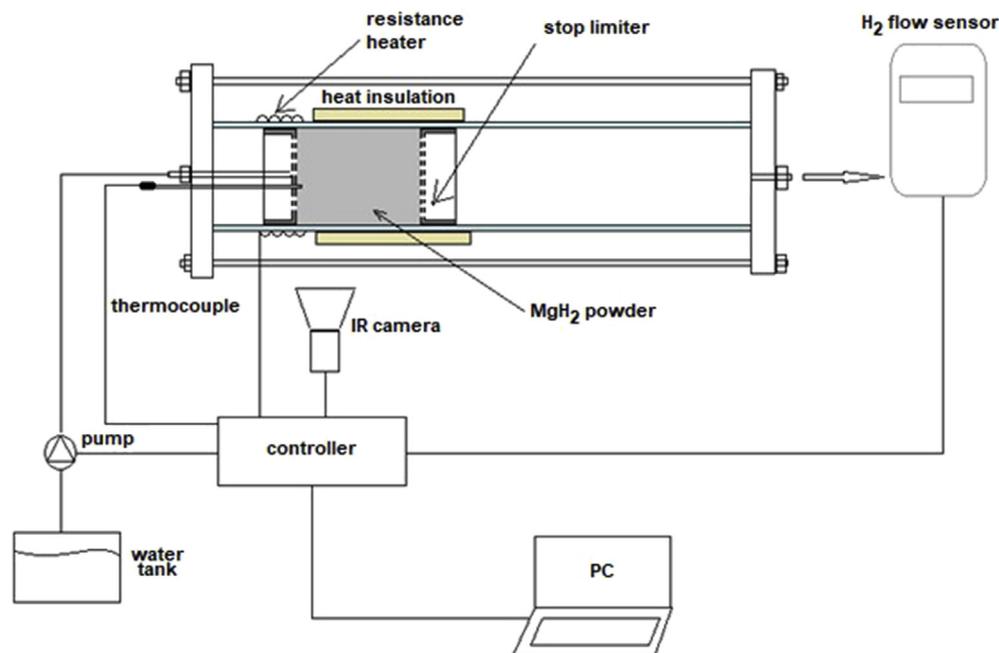
Previously, a series of experiments was carried out to work out the conditions for a controlled and reproducible hydrolysis reaction of magnesium hydride powder with water vapor in order to obtain a controlled flow of hydrogen. The hydrolysis reaction of magnesium hydride is highly exothermic:



Here, the enthalpy  $\Delta H$  depends on what product is formed as a result of the reaction, magnesium oxide or hydroxide. As our experience has shown, the magnesium hydride powders of the above granulometry are rather inert with respect to water. When water is added under normal conditions, vigorous evolution of hydrogen does not occur, the powder slowly hydrolyses for many hours. There is no noticeable increase in

**Table 2 – Granulometric composition of magnesium hydride powder.**

x (μm)	10	15	20	30	40	60	85	120	175	250	350	500
Q(x) [%]	0.3	0.5	1.2	4	7.6	15.9	31	54.4	81.7	93	96.6	100



**Fig. 1** – Diagram of an experimental setup with a quartz tube — a reactor for studying the hydrolysis reaction of magnesium hydride powder with water at temperatures above 100°C.

temperature. A different picture is observed when interacting water with finely dispersed (powder was obtained by grinding in an atmosphere of argon 1 bar, in a planetary mill Fritsch Pulverisette 4) of magnesium hydride powder (Table 3).

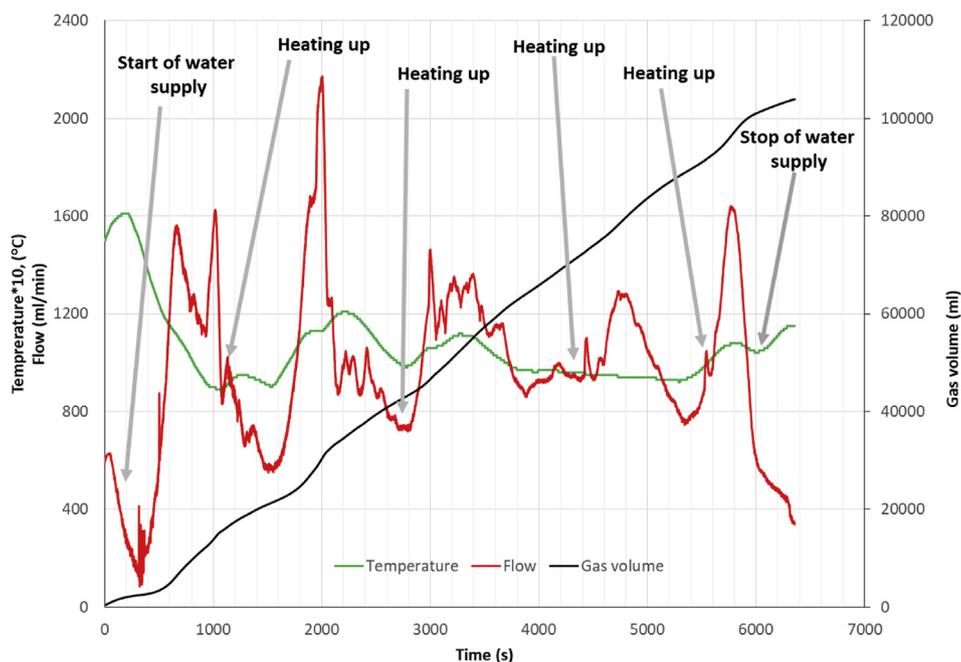
In this case, the powder actively interacts with water and the solution is heated to high temperatures, up to boiling. With increasing water temperature, the hydrolysis reaction is accelerated. To create conditions for the formation of steam and to ensure a high reaction rate, the initial heating of the reaction zone to a temperature above 100 °C is necessary. Heating was provided by a wire resistive heater. Heating control was performed using a thermocouple. The water supply was carried out by a pump, which was operated by the controller, and provided water supply with an adjustable flow rate in the range of 0.2–50 ml/min. The micropump controller was implemented on the basis of the Arduino Leonardo platform. The temperature inside the quartz reactor was controlled by the Flir i7 infrared thermal imager. The flow of hydrogen was measured by a flow sensor: Dwyer GFM2-H2-AVALA2-20L.

To start the hydrolysis process, the left stop-limiter and a small zone of the adjacent magnesium hydride powder were preheated to temperatures of about 110–130°C. Then water was supplied with a constant flow rate in the range of 0.3–0.6 g/min. When a steady stream of hydrogen appeared, manual adjustment of the water supply through the controller was carried out, depending on the amount of hydrogen flow. The resistive heater was periodically turned on or off, also proceeding from the tendency to increase or decrease the

hydrogen flux while taking into account the current water supply by the pump. To obtain data on the temperature distribution inside the quartz reactor, the mobile thermal insulation was shifted to the side and an infrared survey was performed with an assessment of the temperature fields. The process of hydrolysis with steam, with periodic manual adjustment of the water supply and turning on the heater, was carried out until a steady trend towards a decrease in the hydrogen flow was observed and the total amount of hydrogen released approached 90% of the calculated one based on the weight of the loaded powder. Fig. 2 shows a typical example of data obtained at the start and the full carrying out of the process of hydrolysis of 65 g of magnesium hydride powder with steam. Manual adjustment of the water supply and the power of the resistive heater leads to a large irregularity of the hydrogen flow - from 600 to 1600 ml/min, however, the hydrolysis process can be carried out with almost 100% use of magnesium hydride powder and get close to theoretical yield of hydrogen. Despite the fact that the hydrolysis reaction is highly exothermic, in the process of carrying out the reaction it is necessary to periodically turn on the resistive heater in order to compensate for the temperature drop. This circumstance is obviously explained by the fact that the mass of the reacting magnesium hydride is relatively small compared with the mass of the quartz reactor and devices that are in thermal contact with it, and the heat loss through heat conduction and convection exceeds the heat input from the reaction zone.

**Table 3** – Granulometric composition of fine magnesium hydride powder.

x (μm)	0.01	0.05	0.07	0.1	0.2	0.4	0.6	0.8	1	3	5	10
Q(x) [%]	0.1	1.5	7	18	38	56	68	76	88	94	98	100



**Fig. 2** – The change in temperature at the entrance to the quartz reactor, the flow of hydrogen and the total volume of released hydrogen, depending on the time during the hydrolysis of 65 g of magnesium hydride powder. Heating of the reactor and adjustment of the water supply rate was carried out manually.

## Results

To develop a reliable and well-controlled chemical source of hydrogen, it is necessary to answer a number of questions, concerning the structure and extent of the reaction zone, the composition of the reaction products after the reaction zone, in the reaction zone and directly in front of the reaction zone, temperature distribution, water vapor content in the outgoing hydrogen depending on temperature, position of the reaction zone and other factors.

To determine the composition and structure of the reaction products, depending on the distance to and after the center of the reaction zone, the hydrolysis process was stopped when the amount of released hydrogen was about half of the calculated one. After cooling the quartz reactor to a temperature of about 40–50 °C, the reactor was disassembled and the contents of the reactor were carefully removed and divided into five portions of powder. The powder was taken out in layers from the water/steam supply side, each portion was composed of a layer of powder in a reactor about 2 cm long. After infrared drying for 15 min at 150 °C, the mass of each portion of powder was determined, the amount of hydrogen evolved during hydrolysis in an acid solution, microphotographs (x40) were taken. The results are shown in Table 4.

The amount of hydrogen released during the hydrolysis of the first sample is 10 ml and is within the measurement error. This suggests that the first sample consists of a mixture of magnesium oxide and hydroxide. To determine the content of oxide and hydroxide in the sample, the mixture was weighed on an analytical balance, calcined for 1 h at 800 °C in a muffle furnace, and weighed again. Assuming that at 800 °C for 1 h,

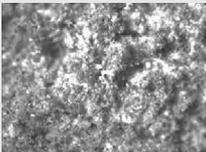
magnesium hydroxide was converted to oxide, the initial composition of the first sample was calculated by weight loss: MgO – 80 wt%, Mg(OH)<sub>2</sub>–20 wt%.

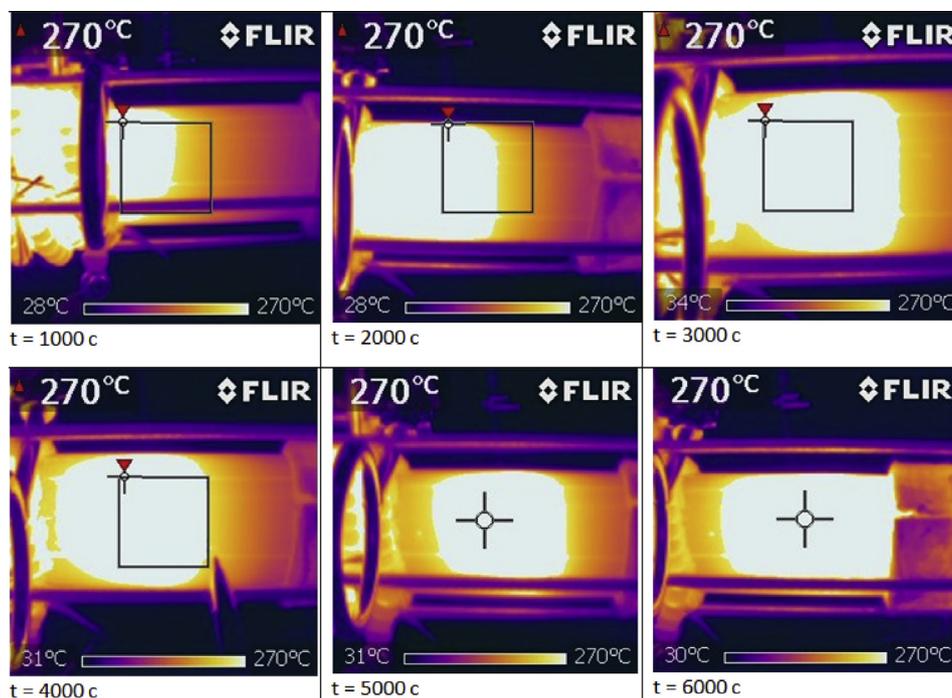
From the obtained data we can draw some conclusions about the nature of the reaction zone of magnesium hydride with water vapor. We assume that the reaction area of the reactor is filled with powder, which absorbs more than 90% of the passing water vapor, which is replaced by evolved hydrogen, and the absorption of water vapor occurs due to the hydrolysis of magnesium hydride and magnesium powder to form a mixture of oxide and magnesium hydroxide. Powder magnesium is formed from magnesium hydride due to the reaction of thermal decomposition of magnesium hydride powder at temperatures in the reaction zone exceeding 350 °C. This definition of the reaction zone allows us to conclude that the reaction zone should be located at least from the middle of the second sample to the middle of the fourth sample and its length is at least 4 cm. It is logical to assume that the main heat release occurs in the reaction zone. The maximum temperature in the reaction zone should occur close to zone center. Improving the thermal insulation of the reaction zone and reducing heat loss can increase the temperature in the reaction zone. Higher temperatures in the reaction zone should lead to its narrowing. That is, the width of the layer of powder where the main absorption of water vapor occurs should decrease.

In order to obtain qualitative information on the heat release in the reaction zone in the process of carrying out the hydrolysis process in a quartz reactor, an IR survey was used (Fig. 3).

When the reactor equipment is loaded, the left edge of the powder load goes 1 cm beyond the right edge of the heating coil, and the right edge of the powder load coincides with the

**Table 4 – The results of the analysis of powder samples on the front of the hydrolysis reaction.**

Sample No	1	2	3	4	5
Appearance					
Microphotograph (x40)					
Weight, g	21.4	20.0	18.6	16.8	13.5
H <sub>2</sub> amount, ml	10	3360	14330	15870	21430
Description	White powder, expanded needle-like crystals and agglomerates with shiny metallic inclusions	White powder with inclusions of gray powder	A mixture of gray and white powder	Gray powder with shiny metallic inclusions. The admixture of white agglomerates of particles	A mixture of gray translucent crystals and gray powder particles



**Fig. 3 – Photos in the IR range of the reaction zone in a quartz reactor during the hydrolysis of magnesium hydride powder with water. White areas indicate zones with temperatures  $>270$  °C.**

left edge of the thermal insulation layer being pushed back. The length of the powder load along the quartz reactor is 10 cm. Thus, based on the above description of the scale, according to the imager, it can be noted that the length of the reaction zone is greatest at the beginning and at the end of the hydrolysis process and is approximately five to 6 cm. In the middle of the hydrolysis process, for the time interval from 3000 to 5000 s, the length of the reaction zone is the smallest - about 4–5 cm. A logical explanation can be offered to the observed patterns. Magnesium hydride powder and reaction products is a porous body and has poor thermal conductivity. At the beginning and at the end of the hydrolysis process, when the reaction zone is at the edge of the powder load, the heat loss from the reaction zone is higher due to the significant contribution of heat sink through radiation. This leads to lower temperatures in the reaction zone, and, consequently, a lower chemical activity of the powder and, accordingly, a larger width of the active interaction zone of steam and magnesium hydride powder.

## Discussion

Images of the temperature distribution in the prototype reactor obtained from an IR camera, as well as data on the dependence of the hydrogen flow on heating, allow the following conclusions:

- the reaction zone has quite clear, pronounced boundaries;
- the main steam flow is spent in the reaction zone, which has a length of 3–5 cm, depending on the temperature distribution: the higher the temperature, the shorter the reaction zone;

- the flat shape of the leading and trailing edges of the reaction zone suggests the possibility of obtaining a stable and constant flow of hydrogen with its smooth increase upon start-up and decline upon completion of the hydrolysis process;
- the organization of the optimal heat balance has a decisive influence on the stability and controllability of the hydrogen flow of the chemical source in question.

From the point of view of the uniformity of the hydrolysis reaction and its controllability, it is necessary to strive to ensure that the temperatures in the reaction zone do not exceed  $350$  °C, when the thermal decomposition of magnesium hydride into magnesium and hydrogen begins. At the same time, on the one hand, because of the thermal decomposition of magnesium hydride, energy is absorbed, and on the other hand, the enthalpy of hydrolysis of magnesium powder is higher, and these thermodynamic processes balance each other. But at the end of the hydrolysis reaction, when most of the powder reacts, a mixture of magnesium powders and magnesium hydride remains, and if we want to maintain a relatively constant level of hydrogen, it is necessary to increase the flow rate of water. In this case, there will be a sharp increase in temperature in the reaction zone, up to temperatures of  $800$ – $900$  °C, which is a dangerous phenomenon in order to preserve the structural integrity of the reactor. From these considerations, it is obvious that the nominal flow of hydrogen is associated with the size and design features of the reactor in which the hydrolysis process is carried out. Of crucial importance is the design of the thermal insulation and thermal management system, which allows maintaining the optimum temperature in the reaction zone and achieving a constant hydrogen flow over time. Undoubtedly, with an

increase in the scale of the system, questions of the structure of the powder, the method of introducing and distributing water vapor into the reactor, as well as the need for introducing pore-forming agents to ensure gas permeability of the powder and reducing pressure gradients will also come to the fore. It is likely that separate engineering solutions will be required for smoothing the flow pulsations and hydrogen pressure. These issues and decisions will be considered in subsequent publications.

## Conclusions

In this paper, we consider the possibility of developing a chemical source of hydrogen based on the hydrolysis of magnesium hydride powder with steam. The proposed design of the hydrolysis reactor and the test bench made it possible to study the peculiarities of the hydrolysis of magnesium hydride powder with water vapor, to obtain estimates of the length of the reaction zone, the complete use of magnesium hydride powder, the composition of the reaction products, the controllability of the hydrogen flow generation.

Based on the data obtained, it can be concluded that it is possible to develop compact and stable chemical sources of hydrogen, based on steam hydrolysis of magnesium hydride powders to create mobile electrochemical power sources based on the conversion of hydrogen into fuel cells into electrical energy.

## Acknowledgement

This work was supported by the Foundation for Assistance to Small Innovative Enterprises in Science and Technology under the Contract No. 38ГC1НТИС5/43235.

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