

ACTIVATED CARBONS FOR HYDROGEN ADSORPTION

L. E. Kanonchik, A. G. Kulakov, D. A. Mishkinis, L. L. Vasiliev
Laboratory of Porous Media
Luikov Heat & Mass Transfer Institute, National Academy of Sciences,
P. Brovka, 15, 220072, Minsk, Belarus
Phone/Fax: (375-17) 284-21-33; E-mail: LVASIL@hmti.ac.by

Abstract

Activated carbon fiber was chosen as an efficient gas (ammonia, methane, hydrogen) sorption material to design a gas storage system. To increase gas sorption capacity a complex compound (activated carbon fiber + chemicals) was applied. The application of a heat pipe in gas accumulator enables one to control the temperature of sorbent bed and provide optimum operational conditions.

KEYWORDS

Carbon, ammonia, methane, hydrogen, heat pipe, sorption, metal hydride/chloride

INTRODUCTION

Hydrogen is the ideal alternative for fossil fuel systems. From environmental point of view, it is the cleanest fuel known until recently, and from economic point of view hydrogen technology will be able to revolutionize the transport and energy market.

Hydrogen is the smallest and lightest molecule known. Among the advantages of hydrogen are its low density and small volume heat of combustion, which leads to the necessity of hydrogen storage in large-sized vessels and cylinders. According to the standard "The US Department of Energy (DOE) Hydrogen Plan" the modern onboard system of hydrogen storage should have capacity of storage 6-7 wt.% at average pressure (2 – 6 MPa) and temperature 273 – 363 K; capacity of 5 kg, and specific energy of 7.2 MJ/kg. None of the existing methods of hydrogen storage is efficient in terms of energy density, of neither a volume nor a mass and gas release rate at same time. From the application point of view it is vital to find the most effective way to store hydrogen and then, to replace the current fuel systems.

Hydrogen storage by solid materials is the most recent system proposed [1]. Initially the research was based on cryogenic systems [2], which are unprofitable from an economic point of view. Recently the studies have focused in the search of the high capacity adsorbent to be used at room temperature. Due to the high density of the adsorbed phase (it corresponds to density of pressurized gas at 60 – 80 MPa) the gas storage capacity in the vessel with sorbent can increase significantly. Since it is close to the liquid density, the volumetric capacity of adsorption system is predicted to be higher than for compression system. Activated carbons, activated carbon fibers and graphite nanofibers are perspective candidates for hydrogen adsorption storage. Many metals, alloys and intermetallic compounds can also reversibly adsorb large amounts of hydrogen. However, none of them is known for the mobile storage pressure-temperature range with ΔH in the range of 15-24 kJ/mol hydrogen.

Our approach is to make composite materials containing two or more different components, in an effort to compensate the limitations of each. Activated carbon fiber with chemicals can be considered as a promising material for hydrogen storage. The objective of this work is to analyze hydrogen storage in several porous carbon-based materials with different porous structures to propose perspective activated carbons (carbon fibers) and metal hydrides compositions for high performance hydrogen storage system. Another interrelated work objective is development of thermally regulated adsorption storage system for dual-fuel (hydrogen and natural gas) automobile. In fact, such gases as methane, ammonia, methanol, etc can be considered as hydrogen storages by itself also.

CARBON MATERIALS AS A STORAGE MEDIUM FOR THE MOST CURRENT GASES

Activated carbon is well known as one of the best adsorbents for gases [3]. In contrast to the chemisorption in metal hydrides [4], the phenomenon of physical adsorption is essentially

accumulation of the undissociated hydrogen molecules on a surface of microporous carbon fibers or particles. This property is due to ability of carbon to be prepared in a very fine powdered or fiber form with highly porous structure and due to specific interactions between carbon atoms and gas molecules. The total amount of adsorbed hydrogen strongly depends on the pore geometry and pore size distribution as well as the storage pressure and temperature. Recently many improvements have been accomplished to obtain microporous carbonaceous materials with extremely high adsorbing properties for different gases [5]. Adsorption of methane and hydrogen are usually takes place in micropores. Macropores have no practically influence on the adsorption capacity, as they are only important for the gas compression and for adsorption/desorption reaction rates [6]. Due to its high surface area and abundant pore volume, activated carbon is considered as good adsorbent. For conventional activated carbon, the hydrogen uptake is proportional to its surface area and pore volume, while, unfortunately, a high hydrogen adsorption capacity (4 ~ 6 wt%) can be only obtained at very low cryogenic temperatures according to theoretical calculations. To gain the goal of the problem – efficient ammonia, methane, and hydrogen storage and transportation it is necessary to develop a high performance microporous adsorbent material and an advanced system of the vessel thermal control.

Thus, the cheap activated carbon fabricated by special thermal treatment of impregnated raw (wood, sawdust, cellulose, straw, paper for recycling, peat etc.) is attractive for modern sorption technologies. The use of specific organic and non-organic compounds as raw impregnates offers production activated carbons with controlled porous structure and high yield (up to 50 wt %). Developed advanced technology allows to produce the homogeneous carbon adsorbents with benzene pore volume 0,3 – 0,6 cm³/g (70 – 80 % - volume of micropores), nitrogen surface area up to 1500 m²/g, iodine adsorption capacity 40 – 70 wt % and methane adsorption capacity up to 160 mg/g (3.5 MPa, 293 K). Impregnated cellulose - containing raw for manufacture special activated carbon materials for ammonia, methane and hydrogen storage systems with high microporosity, surface area and narrow micropore size distribution is the attractive host material for adsorption of different gases. The activated carbon fiber “Busofit” and activated wood-based carbon particles ([7], the Institute of General and Inorganic Chemistry, NASB) fabricated in Belarus are perspective materials for gas storage systems (Figs. 1 – 2).

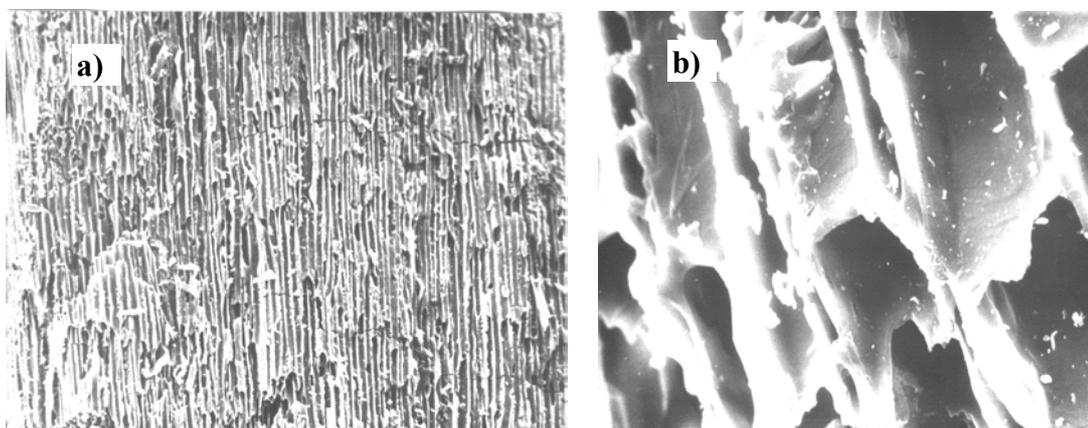


Fig. 1. Active carbon material made from waste wood (IGIC NASB): a) Image multiplied by 30 times; b) by 1000 times

“Busofit” is a universal adsorbent, which is efficient to adsorb different gases (H₂, N₂, O₂, CH₄, and NH₃). Figure 2 shows the texture of the active carbon fiber filament. The carbon fiber refers to microporous sorbents with a developed surface and a complicated bimodal structure. The material can be performed as a loose fibers bed or felt or as monolithic blocks with binder to have a good thermal conductivity along the filament.

In our experiments some samples of activated carbon “Busofit” obtained by the new technology were investigated. The surface area of the commercially available “Busofit” was measured with “Micromeritics AccuSorb 2100” and BET Sorbtometer NOVA and varied from 1140 m²/g up to 1570 m²/g. Now it is clear, that ammonia, methane and hydrogen storage vessels filled with “Busofit” have

certain advantages (for example, methane storage capacity near 170 v/v). To be commercially profitable the adsorption storage is required to have at least 150 v/v. It can be considered as a typical microporous adsorbent with pore diameter near 1 – 2 nm and at the same time as material with high gas permeability.

The micropore distribution is performed mostly on the carbon filament surface. Nowadays a program was undertaken to examine the parameters of an active carbon fiber to optimize both the mass uptake of ammonia, methane and hydrogen and the carbon density.

“Busofit” has such advantages as

- high rate of adsorption and desorption;
- uniform surface pore distribution (0.6-1.6 nm);
- small number of macropores (100-200 nm) with its specific surface area 0.5-2 m²/g;
- small number of mesopores with its specific surface area 50 m²/g.

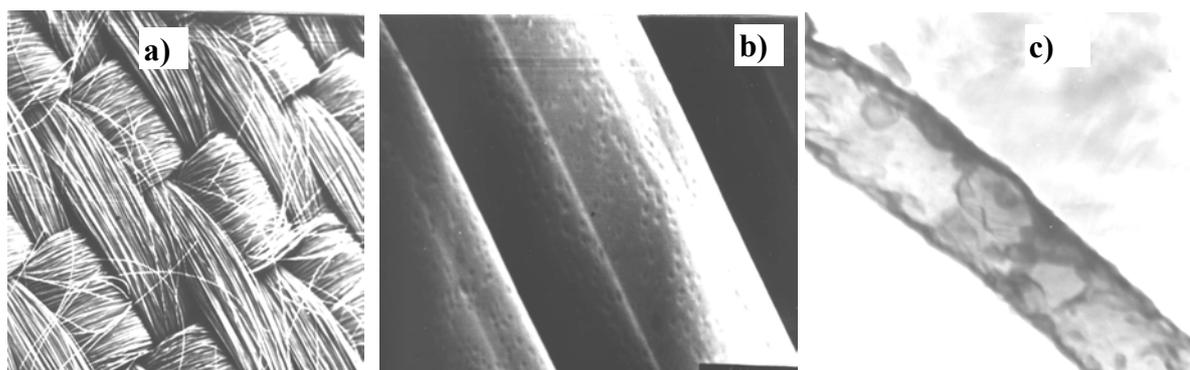


Fig. 2. Active carbon fiber “Busofit”: a) Image multiplied by 50 times; b) by 1000 times; c) by 50000 times

The total volume V , associated with an active carbon adsorbent may be split up into its components:

$$V = V_c + V_v + V_{void} + V_\mu,$$

where V_c – the volume of the carbon atoms of which the adsorbent is composed; V_μ – micropores volume; V_v – meso- and macropores volume; V_{void} – the space inside the vessel free from adsorbent bed. This latter V_{void} can be eliminated by making the solid block of adsorbent.

EXPERIMENTAL RESEARCH OF TEXTURE AND HYDROGEN-SORPTION CAPACITY FOR THE ACTIVATED CARBON MATERIALS

Activated carbon fibers (commercially available “Busofit-AYTM” and modified grades of “Busofit-AYTM”) and granular activated carbon (additionally activated in Luikov Institute Porous Media Laboratory and commercially available) have been used in this work (Table 1). Porous texture of the different materials was all characterized using nitrogen (N₂) physisorption at 77 K and up to a pressure of 0.1 MPa. From the nitrogen physisorption data, obtained with the High Speed Gas Sorption Analyser NOVA 1200, the BET-surface area, total pore volume, microporous volume and t-volume were derived. The BET surface area (S_{BET}) is the surface area of the sorbent according to the model formulated by Brunauer et al. [8] for planar surfaces. The micropore volume is defined as the pore volume of the pores < 2 nm. Microporous volumes calculated from the application of the Dubinin-Radushkevich equation to the N₂ adsorption isotherms at 77 K. The mean pore size of each sample obtained from N₂ adsorption was determined by applying Dubinin-Radushkevich equation. The hydrogen sorption isotherms were measured with the High Speed Gas Sorption Analyser NOVA 1200 at 77 K in the pressure range 0 – 0.1 MPa.

Table 1 summarizes the results of the N₂ and H₂ physisorption measurements of the materials analysed. All samples are highly micro- and mesoporous carbon materials. In our experiments four samples of carbon “Busofit-AYTM” (1 – 4) and three samples of wood-based activated carbon (5 – 7) obtained by new technology were investigated. The activated carbon 207C (8) is made in the Great Britain from coconut shell. Samples 9 and 10 – granular activated carbons, specially developed for effective storage of methane.

Table 1. Textural characteristics and hydrogen-sorption capacities at 77 K and 0.1 MPa for the researched carbon materials

No	Sorbent	a _v , ml/g	a, wt%	S _H , m ² /g	S _{BET} , m ² /g	S _{DR} , m ² /g	V _{DR} , ml/g	V _t , ml/g	R _{DR} , Å
1	Busofit 191-5	199.9	1.76	462	1691	2496	0.887	0.234	49.9
2	Busofit-M2	203.9	1.79	465	1702	2507	0.89	0.43	41.5
3	Busofit-M4	225.1	1.98	536	1715	2547	0.9	0.42	42
4	Busofit-M8	252.9	2.23	571	1939	2985	1.04	0.27	51
5	WAC 97-03	115	1.01	271	715	1050	0.37	0.33	33.4
6	WAC 19-99	172.1	1.51	393	1005	1486	0.53	0.44	41.7
7	WAC 3-00	221.1	1.95	575	1383	2142	0.74	0.22	50
8	207C	209.2	1.84	502	1300	1944	0.69	0.37	41
9	Norit sorbonorit-3	193.8	1.71	458	1361	2044	0.73	0.26	50
10	Sutcliffe	236.6	2.08	527	1925	2864	1.02	0.254	53.6

Remarks: WAC – wood-based active carbon; a_v – volume capacity of hydrogen storage using physisorption, ml/g; a – capacity of hydrogen storage using physisorption, wt%, g/100 g; S_H – BET surface area determined on hydrogen, m²/g; S_{BET} – BET surface area determined on nitrogen, m²/g; S_{DR} – surface area, determined on Dubinin-Radushkevich method, m²/g; V_{DR} – micropore volume, determined on Dubinin-Radushkevich method, ml/g; V_t – mesopore volume, determined on t-method, ml/g; R_{DR} – size of pore, determined on Dubinin-Radushkevich method, Å

According to the offered technology some samples from “Busofit-AYTM” have been prepared by selective thermal processing at high temperature 850 °C. In this way some of the carbon atoms are removed by gasification, which yields a very porous structure. Numerous pores, cracks were formed in the carbon material increasing a specific surface area due to the growth of micropore volume. Additional activation of a sample 1 was carried out at the presence of oxygen. As follows from Table 1 the increase of time of activation from two hours until eight hours in an atmosphere of carbonic gas promotes increase to sorption capacity almost in 1.5 times (samples 2 and 4). The atmosphere of carbonic gas appeared more preferably oxygen for growth of a specific surface and sorption capacity – time of activation of samples 1 and 2 was identical. To increase the adsorbent capacity and the bulk density of material we compressed active carbon fiber together with a binder. Briquet “Busofit” disks have a high effective thermal conductivity and a large surface area. Wood-based carbons (5 – 7) were produced by controlled pyrolysis of waste wood and special activation.

As seen in Table 1, the greatest values of a surface area and micropore volume among carbon fibrous materials has “Busofit-M8”; from wood-based activated carbons it is stand out “WAC 3-00”, from granular carbons – “Sutcliffe”.

The approach of research institutes AGLARG [9] was used for an operative estimation of gas sorption capacity for carbon sorbents. According to it micropore volume and the specific surface area have been chosen as determining parameters. To obtain the function approximating dependence of hydrogen sorption capacity on carbon materials from value of a specific surface area (at pressure 0.1 MPa and temperature 77 K), we used our experimental data (Table 1) and an experimental database (Table 2) of group of institutes - Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University [10].

A test matrix of about 20 different carbon samples, including commercial carbon fibers and fiber composites, graphite nanofibers, carbon nanowebs and single walled carbon nanotubes was assembled. The sorbents were chosen to represent a large variation in surface areas and micropore volumes. Both non-porous materials, such as graphites, and microporous sorbents, such as activated carbons, were

selected. Characterization via N₂ adsorption at 77 K was conducted on the majority of the samples; for this a Quantachrome Autosorb-1 system was used. The results of the N₂ and H₂ physisorption measurements are shown in Table 2. In the table CNF is used to designate carbon nanofibers, ACF is used for activated carbon fibers and AC for activated carbon.

Table 2. Textural characteristics and hydrogen-sorption capacities at 77 K and 0.1 MPa for carbonaceous materials [10]

No	Sorbent	S _{BET} , m ² /g	V _{DR} , ml/g	a _v , ml/g	a _{v, meso} , ml/g	a _{v, micro} , ml/g
1	Synthetic graphite	7	0.00	0	0	0
2	Large-diameter CNF	49	0.01	6	2	4
3	Activated graphite 100	119	0.02	14	6	8
4	Medium-diameter CNF1	120	0.00	12	11	1
5	ACF 400	883	0.34	143	1	142
6	ACF 1200	899	0.37	184	1	183
7	AC Norit 990721	988	0.43	142	2	140
8	AC Norit ROZ 3	287	0.05	36	6	28
9	Activated graphite 300	287	0.05	36	16	19
10	Medium-diameter CNF2	65	0.00	7	7	0
11	AC Norit SX 2	841	0.27	150	17	133
12	ACF 500	988	0.40	142	15	127
13	AC Norit UOK A	1195	0.47	188	10	178
14	AC Norit SX 1	922	0.31	168	18	150
15	AC Norit SX 1G AIR	1030	0.36	171	16	155
16	AC Norit GSX	933	0.26	161	27	134
17	AC Norit SX plus	1051	0.35	165	21	144
18	AC Norit SX 1 G	1176	0.40	187	20	167
19	AC Norit 990293	2029	0.92	238	7	231
20	AC Norit Darco KB	1462	0.42	146	54	92
21	Hyperion CNF	238	0.00	22	22	0

For carbon samples we have found linear relationship between BET surface area and volume sorption capacity of hydrogen at 77 K and 0.1 MPa as:

$$a_v = 0.0783 S_{BET} + 84.02 \quad (1)$$

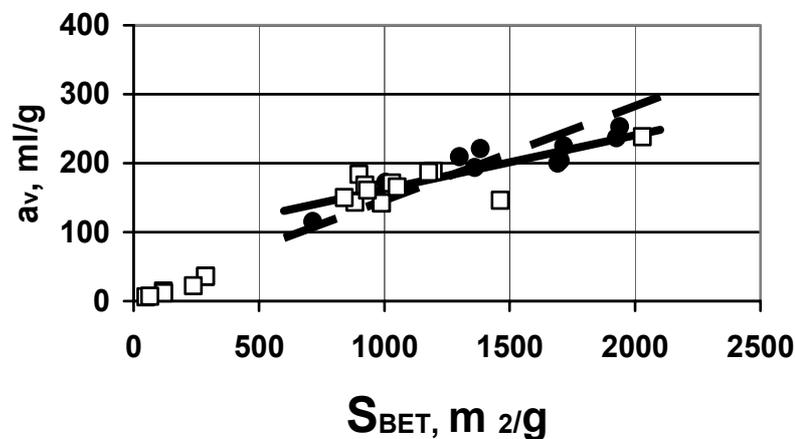


Fig. 3. Volume capacity of hydrogen storage for carbon sorbents vs. BET surface area at pressure 0.1 MPa and 77 K: ● – experimental data (Table 1), a continuous line – the linear approximation obtained by authors; □ – experimental data (Table 2), a dashed line – the linear approximation given in [10]

Figure 3 shows all experimental data and variants of approximation. It is possible to see that our linear correlation fairly good describes all results except for the literature data which correspond to materials with low values hydrogen sorption capacity ($a_v < 50$ ml/g).

Influence of micropore volume on sorption capacity of hydrogen for various carbon materials under the chosen conditions (77 K, 0.1 MPa) is well described by the following linear correlation:

$$a_v = 119.12V_{DR} + 115.41 \quad (2)$$

From Fig. 4 it can be concluded that this correlation does not apply to the carbon samples with low values sorption capacity of hydrogen ($a_v < 50$ ml/g). "Hydrogen" sorbent should have maximum high value of a specific surface area and maximum narrow distribution of micropores.

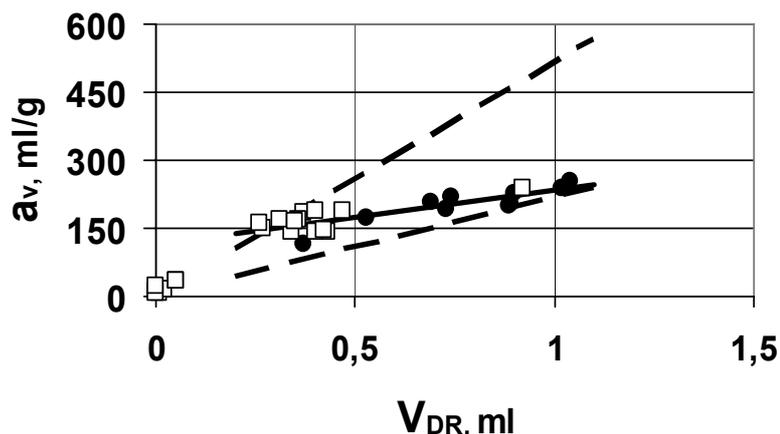


Fig. 4. Volume capacity of hydrogen storage for carbon sorbents vs. micropore volume (determined on Dubinin-Radushkevich method) at pressure 0.1 MPa and 77 K: ● – experimental data (Table 1), a continuous line – the linear approximation obtained by authors; □ – experimental data (Table 2), a dashed line – the linear approximation given in [10]

As follows from Table 1, sorbents "Busofit-M8", "Sutcliff" have micropore volume more than 1 ml/g. They are also the best storage systems for hydrogen (accordingly 253 ml(STP)/g and 237 ml(STP)/g) due to physisorption. Our results demonstrate that a large capacity of adsorbed hydrogen by physisorption under chosen conditions is obtained with sorbents containing a large volume of micropores and a high BET surface area. Optimization of sorbent and sorption conditions is expected to lead to storage capacity of 500–600 ml(STP)/g, close to targets set for mobile applications.

THE ANALYSIS OF ISOTHERMS OF GAS SORPTION ON CARBON MATERIALS

Experimental set-up

The analysis of isotherms of gas at the temperature interval 233 – 293 K and pressure interval 0.1 – 6 MPa was realized by the gravimetric control of the sample (200 – 400 g) during adsorption/desorption cycle. The experimental set-up is shown on Fig. 5. The full amount of the adsorbate was measured. The cylindrical experimental rig of 47 mm inner diameter and 540 mm length was used to simulate full-scale conditions of the experiment. This experimental rig was made from the stainless steel and served as a simulator of the real vessel in the ratio 1:50. Thermocouples were attached to the sample through the sorbent bed (12.5 mm thick). Pressure sensor was used for pressure measurements in the experimental chamber.

Hydrogen and methane isotherms for a high surface activated carbons

The rate of the adsorption/desorption of different gases (ammonia, methane, hydrogen) on the surface of "Busofit" can be evaluated by the isotherms analysis at different temperatures of the sorbent bed. In order to study the sorption capacity of the adsorbent it is necessary to know the quantity of gas

adsorbed on each point of the cycle. There is a general need to have a good fit of experimental isotherms and temperature and to extrapolate some isotherms beside the experimental field. For the carbon fiber “Busofit” the approach of Dubinin is well adapted and allows linking quite simply the physical properties of “Busofit” to the capacity of adsorption of the carbon fiber. Methane isotherms evolution during the cycle of adsorption/desorption of “Busofit AYTM” [11, 12] is shown on Fig. 6. Based on these data we can conclude that “Busofit-AYTM” is competitive to best activated carbons with methane adsorption capacity 113 – 135 g/g at 273 K.

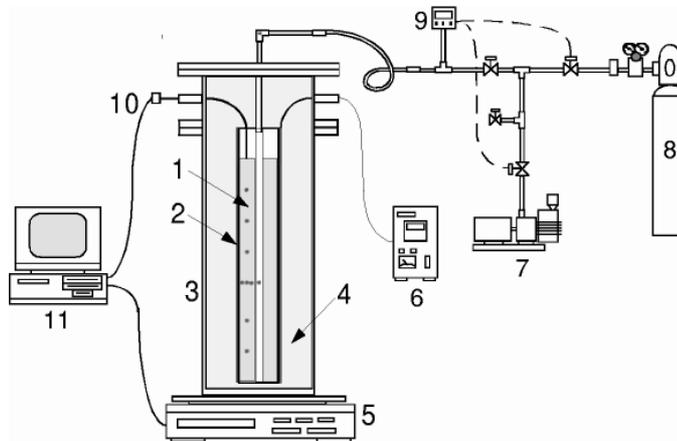


Fig. 5. Experimental apparatus: 1 – reactor bed, 2 – reactor tube, 3 – reactor vessel, 4 – insulation, 5 – balance, 6 – heating controller, 7 – vacuum pump, 8 – H₂ vessel, 9 – pressure regulation system, 10 – thermocouples, 11 – personal computer

As an example, Fig. 7 shows the experimental isotherms of the adsorption and desorption of hydrogen on carbon fiber “Busofit-M8” and wood-based activated carbon “WAC 3-00” at the nitrogen temperature. Absence of an appreciable hysteresis confirms that reversible physisorption exclusively takes place with all investigated materials.

Physisorption on microporous carbons can be described with the Dubinin-Radushkevich equation [13]

$$a_{eq} = \frac{W_0}{v_a} \exp \left\{ - \left[\frac{R_\mu T \ln(P_{sat} / P)}{E} \right]^2 \right\}. \quad (3)$$

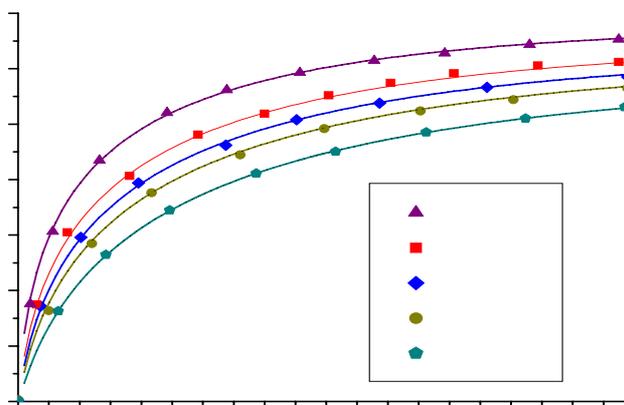


Fig. 6. Methane sorption isotherms for active carbon fiber “Busofit”: experimental data – points; calculated data (Dubinin-Radushkevich equation) – lines

The theory of microporous volume filling, worked out by Dubinin, is widely used for quantitative characteristic of adsorptive properties and basic varieties of porous structure. Equilibrium state equation (3) includes the saturation pressure P_{sat} . Since the hydrogen sorption isotherms are measured within the temperature and pressure intervals comprising the regions of supercritical states of the adsorptive ($T_{cr} = 33.24 \text{ K}$ $P_{cr} = 1.298 \text{ MPa}$), the notion of saturation pressure loses its physical meaning. In the work [14] the saturation pressure is determined by the formula:

$$P_{sat} = P_{cr} (T / T_{cr})^2 \quad (4)$$

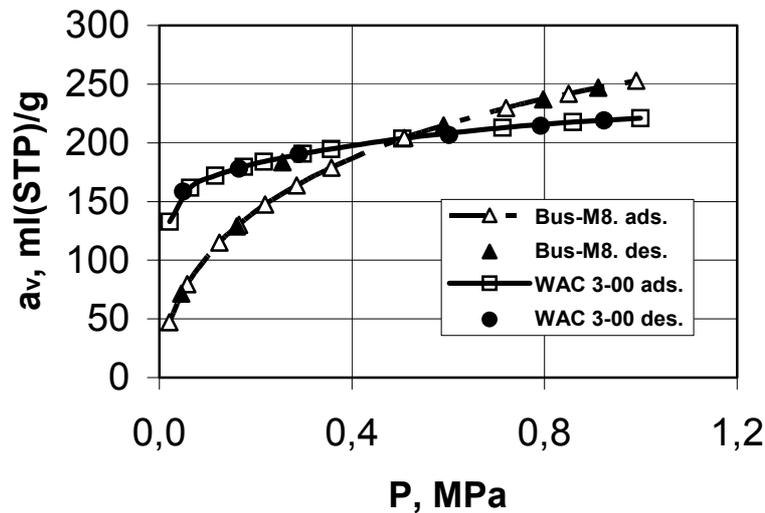


Fig. 7. Isotherms of hydrogen adsorption and desorption on carbon materials at temperature 77 K, measured by the High Speed Gas Sorption Analyser NOVA 1200

As a results of the experiments, we obtained hydrogen sorption isotherms for different carbon materials and empirical coefficients for the Dubinin-Radushkevich equation (5), presented in Table 3.

Table 3. The empirical coefficients of Dubinin-Radushkevich equation for hydrogen sorption on the carbon materials

Material	$W_0, \text{ ml/g}$	$E, \text{ J/g}$
Busofit-M2	369	1783
Busofit-M4	376	1922
Busofit-M8	482	1710
Sutcliffe	453	1699
WAC 3-00	270	3782
207 C	343	1969

With the purpose of a choice of the most suitable sorbent of hydrogen, isotherms (Fig. 8) of studied materials were compared at a level of pressure 3.5-6 MPa, representing practical interest for development of onboard storage system. It is obvious, that the best sorbent in the field of nitrogen temperature – the activated fiber "Busofit-M8", having major effective porosity (0.78), bulk density of 500 kg/m^3 and an advanced surface area ($2985 \text{ m}^2/\text{g}$).

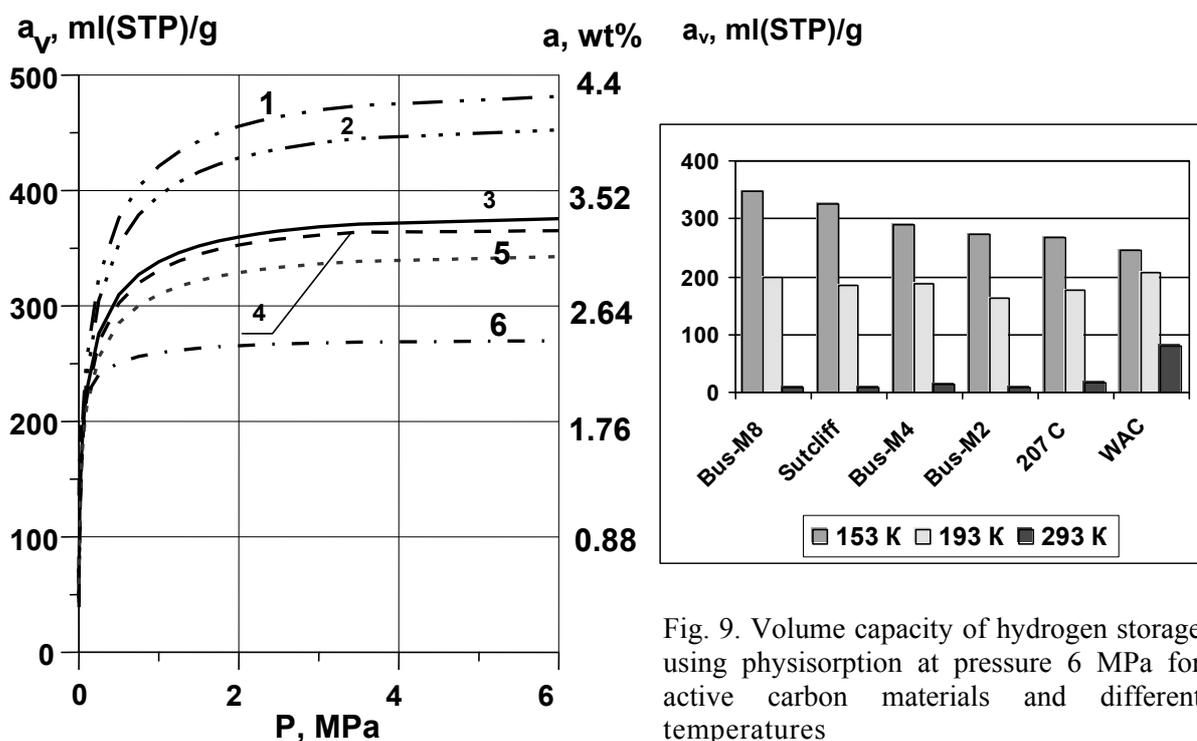


Fig. 8. Hydrogen sorption isotherms for the temperature 77 K and different carbon materials: 1 – “Busofit-M8”, 2 – “Sutcliff”, 3 – “Busofit-M4”, 4 – “Busofit-M2”, 5 – 207 C, 6 – “WAC 3-00”

At pressure 6 MPa "Busofit-M8" reaches storage capacity up to 482 ml/g. Apparently, that 8-hours post-treatment of a carbon fiber by carbonic gas enhanced both microstructural, and the surface characteristics of the original "Busofit". As a result, the hydrogen sorption of a carbon fiber at cryogenic temperatures was improved almost twice, in comparison with samples "Busofit-M2" and "Busofit-M4" whose activation was prolonged a smaller time. From the analysis of physisorption isotherms (Fig. 8) follows, that the wood-based carbon ("WAC 3-00") with the greater specific surface area ($S_{BET}=1382 \text{ m}^2/\text{g}$) immerses the smaller amount of hydrogen and its isotherm lays below an isotherm of carbon 207C with a specific surface area equal to $1300 \text{ m}^2/\text{g}$. The similar "abnormal" behaviour testifies more advanced secondary structure meso- and macropores. Here it is important to realize that hydrogen does not exclusively adsorb in the micropores but also on the surface of the mesopores.

A summary of the results on volumetric capacity of storage of hydrogen for the investigated materials is given on Fig. 9. It is observed that the H_2 uptakes are very low at room temperature and pressure 6 MPa for all carbon samples, but the wood-based material of large surface area has the best sorption characteristics – storage capacity equal of 80 ml(STP)/g.

The influence of temperature can be seen on Figs. 9 – 10. The storage capability is increasing for lower temperatures. Figure 11 compares the behaviour of the adsorption isotherms at different temperature levels for two of the more promising samples: steam activated “Busofit-M8” and wood-based carbon “WAC 3-00”. The shape of the isotherms in the two cases is dissimilar. The isotherms for the 77 and 153 K exhibit a classical type 1 isotherm shape indicating a microporous material. The isotherms at room temperature exhibit a much less pronounced curvature (more like type II isotherm). As is seen from plots (Fig. 6, Fig. 10) experimental data fit the calculated adsorption values (Dubinin-Radushkevich equation) with an error sufficient for practical purposes.

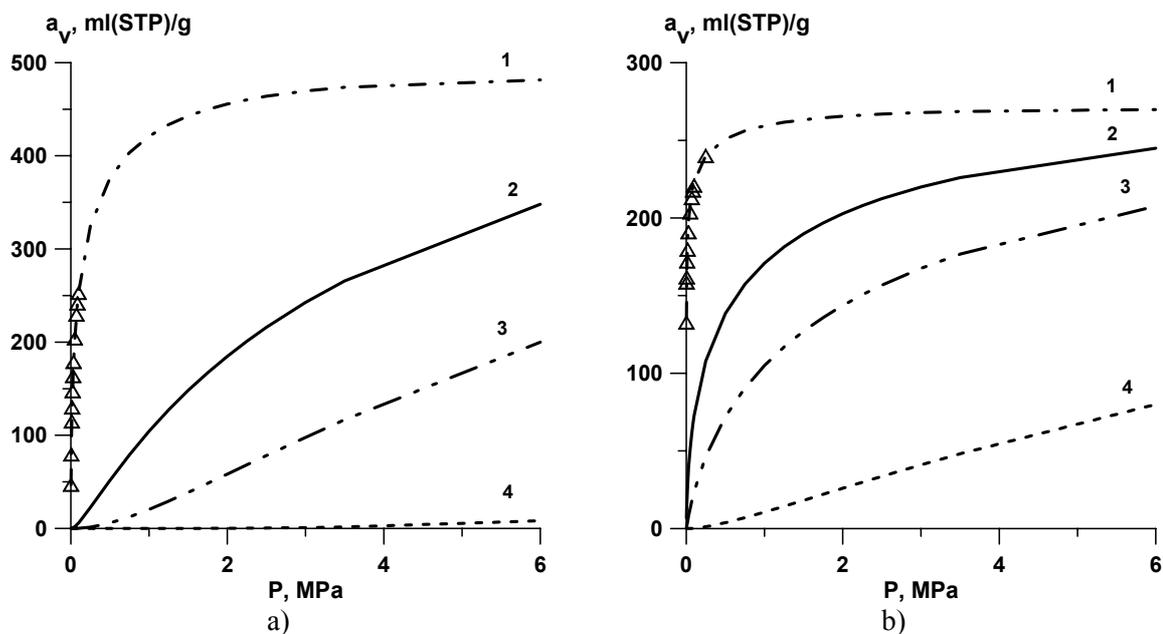


Fig. 10. Hydrogen adsorption isotherms for active carbon fiber “Busofit-M8 ” (a), wood-based carbon “WAC 3-00” (b) and different temperatures (1 – 77, 2 – 153, 3 – 193, 4 – 293 K): experimental data – points, calculated data (Dubinin-Radushkevich equation) – lines

ACTIVE CARBON FIBER AND CHEMICAL COMPONENTS

To minimize a void space and increase the adsorbent capacity of the active carbon fiber we need to compress “Busofit” together with a binder. The combination of the carbon material and metal hydride or/and chloride microcrystals disposed in the same volume, can be possible solution for problem of efficient gas storage and transportation.

The sorbent complex compound microstructure obtained has been studied using Scanning Electro Microscope (SEM). The characterization should reveal a porous structure with a uniform distribution of salts without formation of agglomerates or distribution of particles with different dimensions [15]. Fig. 11 shows that the structure of the salt around the fiber is porous which is favorable for heat and mass transfer.

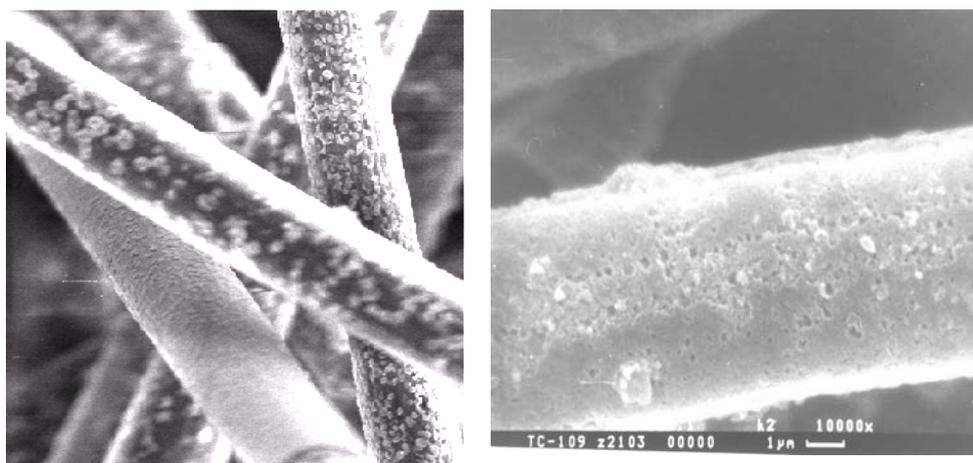


Fig. 11. “Busofit” filaments covered by CaCl_2 microcrystals. Image multiplied by 10000 times and 50000 times

The results of the experimental analysis of the sorption capacity of the active carbon fiber “Busofit” and fiber “Busofit” + chemicals are presented in the Table 4; the data are obtained for the room

temperature, except methane (253 K). Figure 12 shows ammonia sorption isotherms for the active carbon fiber “Busofit” and complex compound “Busofit+ CaCl₂”.

Table 4. Full sorption capacity of a sorbent bed

Full sorption capacity of the sorbent bed	“Busofit”	“Busofit” + CaCl ₂ or “Busofit” + LaNi _{4.5} Al _{0.29} Mn _{0.21}
Methane, T = 253 K, P = 6 MPa	182 v/v	
Ammonia, g/g	0.35	0.62 – 1.03
Hydrogen, wt%	1.5	3.2
Methanol, g/g	0.55	

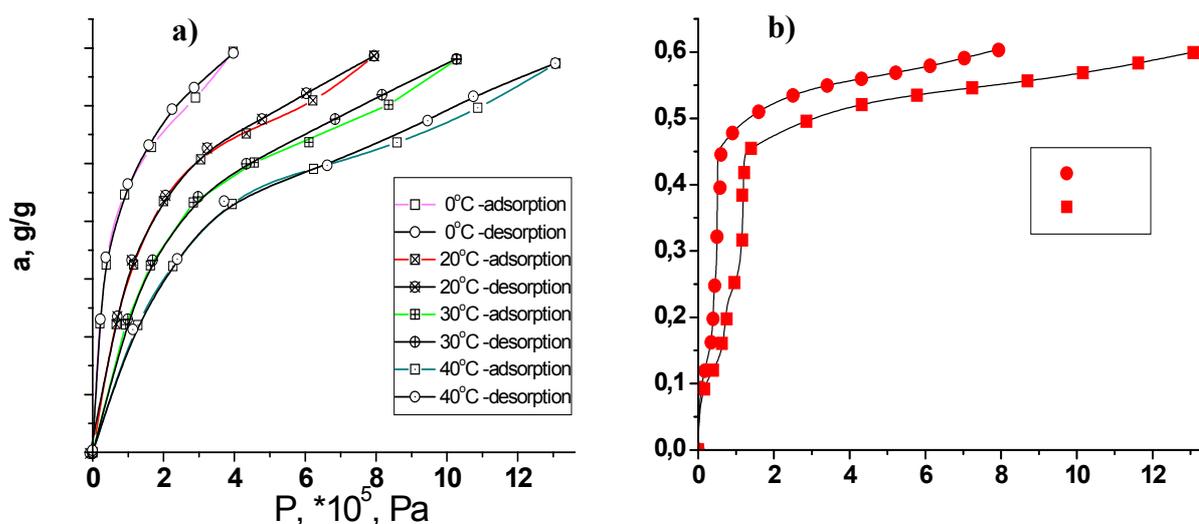


Fig. 12. Ammonia sorption isotherms for “Busofit” (a) and “Busofit+ CaCl₂” (b).

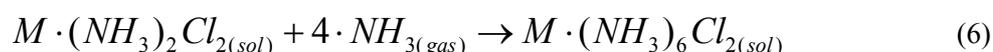
For “Busofit” it is typical a micropore distribution mostly on the filament surface. A set of microcrystals of metal hydrides/chlorides is attached on the filament surface also. Combination “Busofit” + metal hydrides have some particularities to compare with the combination “Busofit” + metal chlorides. Due to the high density of metal hydrides, the systems tend to be very compact, minimizing precious volume and envelope. However, the relatively low hydrogen capacity of metal hydrides tends to make the systems heavy. Thus, metal hydride applications are best suited for systems where power and volume are more critical than weight. A hydrogen compressor, or storage reservoir based on a reversible solid sorption will be attractive if the process can store high gas density. For that, the reactor must contain a large quantity of reactive mixture and the kinetics of the gas-solid reaction will be sufficiently fast. Heat and mass transfer must be efficient, which implies good porosity and high thermal conductivity of the reactor material. In the case of gas-salt reaction, the use of a salt-binder mixture (carbon, exfoliated graphite, graphite intercalation compounds and intercalated or impregnated carbon fibers) enhanced the energy and power performances of the system. Another solution is the use of impregnated carbon fabrics saturated by metal hydrides. Successful application in practical systems requires particular properties of the hydride alloys. Good alloy candidates (Table 5) must have relevant temperature and pressure interval. High energy density, which allows volume and/or weight optimisation of given storage system, is required. The pressure plateau must also be inside of the system operational range.

Metal hydride reaction inside the storage vessel can be thermally controlled (for instance, by heat pipe heat transfer devices), or pressure controlled (isobaric conditions).

During adsorption the stage solid material (metal chloride/hydride) reacts with the gas accordingly with following exothermic reaction:



Practically, this chemical reaction is equilibrium, and for example, in the case of transition metal chloride MCl_2 (S) and ammonia (G), the following reaction can be observed:



The enthalpy of reaction ΔH_{react} in (5) is about 50 kJ/NH₃ mol. for heating. The poor thermal conductivity of the solid salt (about 0.1 W/(m·K)) and the very high expansion factor of the salt S during its reaction with the gas G , are two critical parameters being able to reduce the sorption capacity and reaction rate. Heat has to be evacuated outside during the chemical reaction of adsorption, and gas diffusion has not to be suppressed to reach the salt molecules. Conversely, in the desorption phase, the reactor operates as regenerator in an endothermic reaction.

The use of additives (active carbon fiber) to metal chloride/hydride has two functions:

- the increase of the total sorption capacity (adsorption + chemisorption)
- the increase of the thermal conduction of the reactant and of the heat transfer coefficient at the interface between reactant and wall,
- the maintenance of a high porosity and permeability of the medium during the solid-gas reaction.

The addition to metal chloride/hydride of carbon powders, graphite compounds, expanded graphite, activated carbons, carbon fibers, carbon fabrics and felts have enhanced the performances of the gas storage vessel. It is particularly convenient to use carbon fabrics because they possess the following main qualities:

- 2D high thermal conduction (if the precursor fibers have good thermal conductivity),
- high gas permeability into the inter-fibers space,
- possibility to provide good thermal contact between sorbent bed and the heat exchanger/reactor wall.

The metal hydride + “Busofit” gas storage vessel can also be considered as a heat sink for the transport vehicle, or the source of energy, for instance, for the air conditioning system. The heat sink absorbs and rejects metabolic, sun and equipment heat loads generated during the car traffic. Table 5 contains some of the low temperature metal hydrides.

Table 5. Metal hydride materials for the hydrogen storage and transportation

Metal hydride	Suitable as sorbent	Technical storage capacity, wt%	Temperature, K
LaNi _{4.1} Al _{0.52} Mn _{0.37}	Yes	0.7 – 0.9	430 – 490
LaNi _{4.5} Al _{0.29} Mn _{0.21}	Yes	0.8 – 1.0	373 – 433
LmNi _{4.91} Sn _{0.15}	Yes	1.0	279 – 303
Ti _{0.9} Zr _{0.10} V _{0.43} Fe _{0.09} Cr _{0.09} Mn _{1.5}	Yes	1.0	283 – 323
Ti _{0.99} Zr _{0.01} V _{0.43} Fe _{0.09} Cr _{0.05} Mn _{1.5}	Yes	1.0	268 – 303

HEAT TRANSFER IN THE SORBENT BED

Carbon material can be used as a compact "sandwich" with cylindrical or flat heat pipes, applied as thermal control systems. The dynamic mathematical thermal model of the sorbent bed (Fig. 13) has following constituents [12, 16]:

- 1) Dubinin and Radushkevich equation (3) of the state of gas;
- 2) the equation of energy:

$$r(\varepsilon c C_g + \rho C + \rho a C_a) \frac{\partial T}{\partial \tau} + r c v C_g \frac{\partial T}{\partial r} = \frac{\partial}{\partial r} \left(r \lambda \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(r \lambda \frac{\partial T}{\partial z} \right) + r q_{st} \rho \frac{\partial a}{\partial \tau}, \quad (7)$$

where the isosteric heat of desorption is: $q_{st} = R_{\mu} T \left[\frac{\partial \ln P}{\partial \ln T} \right]_{a=const}$; (8)

3) the equation of continuity:

$$r \frac{\partial}{\partial \tau} (\varepsilon c + \rho a) + \frac{\partial}{\partial z} (rcv) = 0; \quad (9)$$

4) the equation of kinetic of sorption:

$$\frac{da}{d\tau} = K_{so} \exp\left(-\frac{E}{R_{\mu} T}\right) (a_{eq} - a), \quad (10)$$

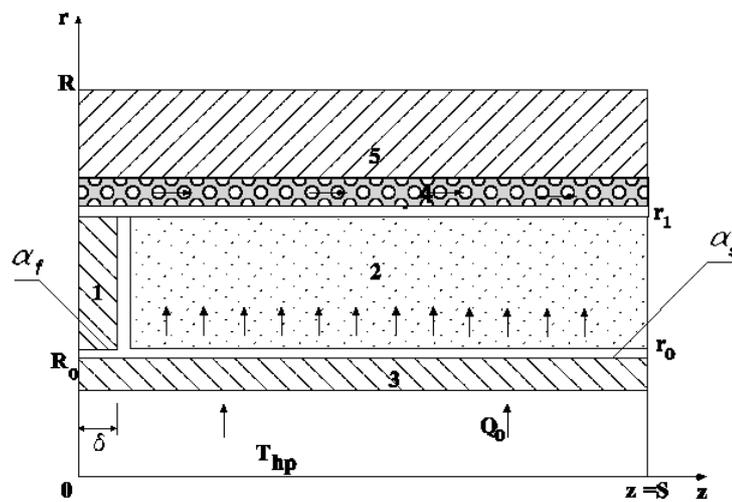


Fig. 13. Diagram of the calculated element of the SSH: 1 – fin; 2 – sorber; 3 – shell of the heating element; 4 – channel for gas discharge formed by the perforated tube and the cylinder body; 5 – cylinder body

where $K_{s0} = 15D_{s0} / R_p^2$, R_p - radii of the particle. D_{s0} – constant necessary to determine the coefficient of a surface diffusion, $D_s = D_{s0} \exp\left[E / (R_{\mu} T)\right]$

The solution was found for the fixed gas flow from the SSH vessel

$$2\pi \frac{d}{d\tau} \int_{\delta}^{L_1} \int_{r_0}^{r_1} (\varepsilon c + \rho a) r dr dz = -g / N \quad (11)$$

with boundary conditions:

$$P|_{\tau=0} = P_0; \quad T(r, z)|_{\tau=0} = T_0(r, z) = T_{env}; \quad (12)$$

$$\frac{\partial T}{\partial z} \Big|_{z=0} = 0, \quad \frac{\partial T}{\partial z} \Big|_{z=S} = 0; \quad -\lambda \frac{\partial T}{\partial r} \Big|_{r=R} = \alpha_{env} (T - T_{env}), \quad (13)$$

$$-\lambda \frac{\partial T}{\partial r} \Big|_{r=R_0} = \frac{Q_{hp}}{2\pi R_0 SN}, \text{ or } T \Big|_{r=R_0} = T_{hp}, \quad (14)$$

where Q_{hp} - heat flow used to heat one cylinder of the vessel, T_{hp} - gas vessel wall temperature.

The first condition (14) corresponds to the situation where the power Q_{hp} is known, and the second condition corresponds to the situation where the heating power is not limited and the temperature T_{hp} is set. This temperature is maintained at the inner surface of the heat pipe due to the contact of its evaporation zone with a large heated body, such as an engine. To solve the set of equations (3, 7 – 10) with boundary conditions (12 – 14) the method of finite elements was chosen.

The suggested simple model gives us a possibility to obtain the field of temperature and gas concentrations during charge-discharge (adsorption/desorption) procedures of the gas vessel. A set of calculations was performed for the high-surface area activated carbon fiber “Busofit-M8” and wood-based carbon “WAC 3-00” as promising gas sorption materials to design a hydrogen storage system. Figure 14 shows the plots of the volume storage density of hydrogen in the vessel (50 l) as a function of the

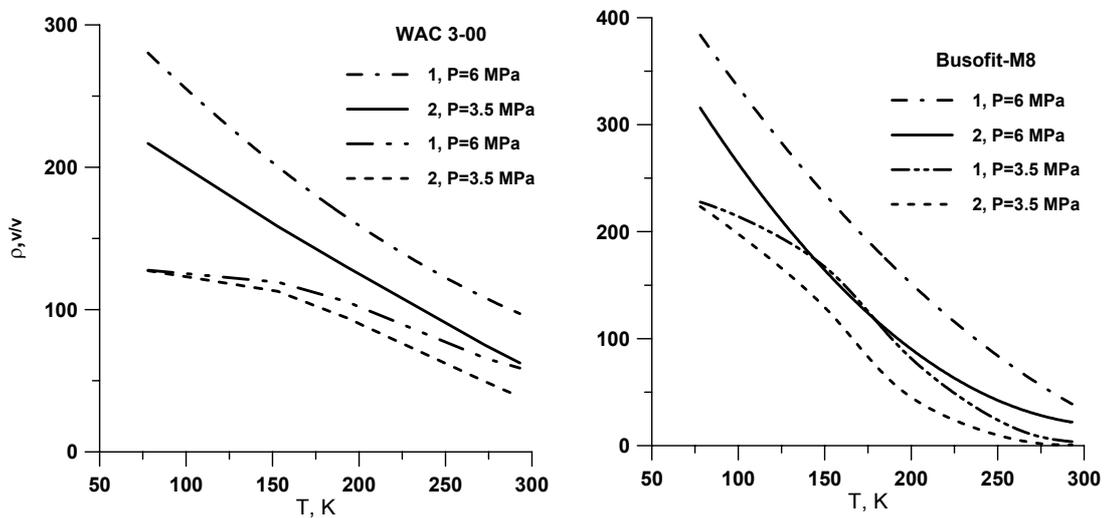


Fig. 14. Volume storage density of hydrogen (1 – the adsorbed and compressed gases; 2 – the adsorbed phase) vs. temperature for different pressure: $P = 6$ MPa and 3.5 MPa

temperature. It is evident that it is necessary to take into account the presence of the compressed gas in the adsorbed storage system at pressures 3.5-6 MPa, the compressed fraction can be measured up to 30 – 50 %. The maximum volume storage density of hydrogen was 380 v/v at 77 K and 6 MPa for “Busofit”. It is important, that the whole amount of storage gas was about 180 v/v at 195 K. However, the “WAC 3-00” sample ensured the value 120 v/v at 273 K.

Successful application in practical systems requires particular properties of the hydride alloys. Suitable alloys must also have reasonable kinetics of absorption and desorption. Fast kinetic of desorption is required for operation during the cooling mode. Often it is extremely difficult to recharge the alloy to its fully hydride state due to unfavourable absorption kinetics. It may be even impractical to regenerate the material after use for some applications.

HEAT PIPE HEAT EXCHANGERS

The efficient system to perform a sorbent bed thermal control during its charging/discharging is heat pipe heat exchanger. “Busofit” can be used as a compact sandwich with flat, or cylindrical heat pipes being in good thermal contact with the surrounding, or source of energy (for example, gas flame, electric heater). Flat heat pipe panels (HPP) have some advantages over conventional cylindrical heat pipes, such as geometry adaptation, ability for localized heat dissipation and the maintenance of an entirely flat isothermal surface. The liquid-vapour interface formed in capillary channels inside the

heat pipe panel is capable to generate self-sustained thermally driven oscillations. Thin layer (several mm) of the sorbent composite (for example, active carbon powder + salts) between mini-fins on the outer side of the heat pipe panel ensures an advanced heat and mass transfer during the cycle adsorption/desorption.

This device is filled partially with working fluid. The flow instabilities inside of this device are produced due to the heat input in one part of it and heat output from the another part by heating multi-channels ($H = 2\text{ mm}$, $L = 5\text{ mm}$) at one end and simultaneously cooling the other end thus resulting in pulsating fluid. This heat input and output stimulates a heat transfer, as a combination of sensible and latent heat portions. The flow instabilities are a superposition of various underlying effects.

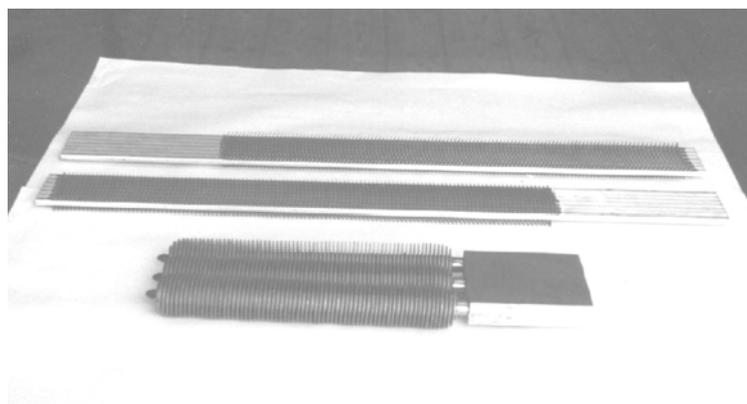


Fig. 15. Heat pipe panels (pulsating heat pipe) for sorbent bed thermal control

In our experiments as an experimental set-up an aluminium multi-channel panel was chosen. The main parameters of flat aluminium heat pipe panel, developed in the Luikov Institute are: HPP width - 70mm, HPP height - 7 mm, HPP length - 700 mm, evaporator length - 98 mm, condenser length - 500 mm, mass- 0, 43 kg. Propane was applied to fill the HPP and it is interesting as a working fluid with the point of view of its compatibility with all heat pipe envelopes and wick materials (aluminium, steel, stainless steel, copper, AL_2O_3 , et al.). The typical heat pipe panel for sorbent bed thermal control is shown on Fig. 15.

CONCLUSIONS

To improve the parameters of the gas storage system the activated carbon fiber and metal hydride/chloride with the binder was suggested. Original sorption capacity data for novel composite materials were obtained. The use of a thermo-chemical material based on carbon nano-fibers in a solid sorption reactor promises a good perspective for design a new type of gas storage systems.

Acknowledgments

Research supported by the Program of focused basic Researches “Hydrogen Energy” of National Academy of Sciences of Belarus; project No “Hydrogen 13”

Nomenclature

a , current, or nonequilibrium, adsorption, kg/kg; c , density of free gas, kg/m^3 ; C , specific mass heat of the sorbent skeleton, $\text{J}/(\text{kg}\cdot\text{K})$; C_g , specific mass heat of the free gas, $\text{J}/(\text{kg}\cdot\text{K})$; C_a , heat capacity of the adsorbed methane, $\text{J}/(\text{kg}\cdot\text{K})$; E , activation energy, J/kg ; G , mass flow rate of the gas flowing out of the cylinder, kg/sec , g/sec ; g_i , mass flow rate of the gas flowing out of the calculated cell of the cylinder, kg/sec ; K_{s0} , preexponential factor in the approximate kinetic equation; m , dynamic coefficient of filling the cylinder; m_e , unwithdrawn gas mass; M , mass of the gas in the cylinder, kg ; M_i , mass of the gas in the calculated cell, kg ; N , number of calculated cells in the cylinder; P , pressure, Pa ; q_{st} , heat of phase transition, or isosteric sorption heat, J/kg ; Q_{hp} , power of heating of the entire cylinder, W ; r and z cylindrical coordinates, m ; R , outside radius of the cylinder shell, m ; R_o , inside radius of the heating-element shell, m ; r_o and r_i , inside and outside radii of the annular layer of the sorbent, m ; R_{ts} , gas constant, $\text{J}/(\text{kg}\cdot\text{K})$; R_p , mean radius of the particles, mm ; T_{hp} , temperature at the inner surface of the

heating-element shell, K, °C; $2S$, finning step, m, mm; T , temperature, K, °C; \bar{T} , mean temperature of the sorbent layer, K; v , component of the velocity vector, m/sec; v_a – specific volume of adsorbed media; V_a , partial molar adsorption volume; V_g , molar gas-phase volume; z_g , coefficient of gas compressibility; α , coefficient of heat transfer, W/(m²-K); ε , porosity determined as a part of the volume occupied by the free gas (not bound by adsorption); 2δ , fin thickness, m, mm; λ_{eff} , effective thermal conductivity of the sorbent layer, W/(m-K); ρ_s , density of the sorbent skeleton, kg/m³; ρ , total density of the free and adsorbed gases in the cylinder, kg/m³; ρ_v , volume density of storage, nm³/m³; τ , time, sec. **Subscripts.** eq, equilibrium conditions; a, adsorbate; cr, critical state; e, finite value; env, environment; hp, heat pipe; 0, initial value; s, sorbent; f, fin; t, transfer.

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