Experimental investigations of thermal processes in the flow-through hydrogen purification reactor

D V Blinov1, V I Borzenko1, D O Dunikov1,2, A N Kazakov1

1 Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 bld. 2, Moscow, 125412 Russia
2 National Research University «Moscow Power Engineering Institute», Krasnokazarmennaya 14, Moscow, 111250 Russia

e-mail: D.V.Blinov.JIHTRAS@yandex.ru, h2lab@mail.ru

Abstract. The paper presents experimental results of thermal processes investigations in flow type metal hydride hydrogen storage and purification reactor RSP-8(I). Thermal processes in the reactor during hydrogen separation from carbon dioxide are studied. Optimal operation parameters for hydrogen purification and performance efficiency of metal hydride reactor RSP-8(I) are defined experimentally. Investigations of heat and mass transfer inside a vertical metal hydride reactor RSP-8(I) with 1 kg of LaFe0.1Mn0.3Ni4.8 show considerable non-uniformity of pressure inside the bed. If the reactor is charged from the top, the hydrogen pressure at the bottom is lower by 0.2-0.3 MPa, which results in earlier occurrence of heat and mass transfer crisis.

Introduction

Nowadays in many countries including Russia much effort is aimed at the increase of renewable energy share. There is increased interest to hydrogen production based on biological methods, the so-called “biohydrogen”. Biohydrogen is considered to be a fuel for transportation means and autonomous power plants based on low temperature fuel cells. The estimations show that 1…10 m3 H2 producing bioreactor can supply 5 kW power plant for several hours. It fully corresponds to the needs of an individual household [1]. Dark fermentation is the most promising among biological hydrogen production methods due to its possibility to utilize different substances including organic wastes, high hydrogen production rate compared to other biological methods, independence of light, and production of valuable by-products [2]. However, direct use of biohydrogen in fuel cell based power plants is impossible because of high content of gaseous impurities, mainly carbon dioxide amounting to 50-70% vol, and low partial pressure of hydrogen, less than 1 bar [3].

Some intermetallic compounds are able to selectively absorb hydrogen with high extraction ratio (75-90%) and desorb ultrapure hydrogen 99.9999% [4-8]. It is challenging way to overcome problems in biohydrogen utilization. Solid phase hydrogen storage and purification systems based on metal hydrides possess reliability, efficiency, and safety [9-11]. However, scaling effect influences physicochemical and thermal properties of hydrogen storage beds in real devices, which use large quantities of metal hydride, more than 100 g. Main research and development problems of hydrogen storage and purification systems unlike the lab scale research of hydrogen absorbing materials are heat and mass transfer processes in hydrogen storage beds [12]. The development of efficient hydrogen storage systems first of all depends on the efficiency of heat and mass transfer for the heat evacuation/supply during hydrogen absorption/desorption. Activated metal hydride in hydrogen storage devices is usually a fine dispersed powder with particle size varied within the range of 1-10 μm and low effective thermal conductivity (0.1-1 W/m K), which depends on the pressure of the filling gas and the hydrogen concentration absorbed in
the particles. Presence of gas impurities in hydrogen leads to a significant change in sorption kinetics and a decrease of device efficiency [13]. System effects in power plants utilizing solid phase hydrogen storage materials are virtually not studied. However, they define energy efficiency of integrated power supply systems based on fuel cells.

Metal hydride reactors for hydrogen storage and purification, which were developed in JIHT RAS, operate in pressure swing adsorption (PSA) manner [5, 6]. However, this method has a number of disadvantages:

1. Necessity of cumbersome valve assemblies;
2. A need to regulate impurity venting process from a free volume of metal hydride reactor;
3. Large hydrogen losses up to 20%, depending on required hydrogen purity;
4. Thermal energy losses during cycle heating/cooling of reactors.

New developed flow-through purification method does not possess these shortcomings [14, 15].

The goal of the present study is to investigate thermal processes in flow-throw hydrogen purification reactors.

1. Experimental details

Experimental investigations of thermal processes were conducted on the experimental test bench 12-04 JIHT RAS with new developed metal hydride reactor RSP-8(I). The scheme of the experiment is presented in figure 1 and consists of gas ramp for preparation of mixtures (1), flow-through metal hydride reactor RSP-8(I) (2), vacuum pump (3), gas analyzer (4), pressure reducer (PR), pressure sensors (PS), gas flow meters (FM) and valves (V).

![Figure 1. The schematic diagram of test bench 12-04 JIHT RAS and RSP-8(I) reactor.](image)

Internal and external heat exchange schemes are calculated using a mathematical model of heat and mass transfer in metal hydride porous beds during sorption/desorption of impure hydrogen, developed jointly with MPEI [16].

The RSP-8(I) reactor has tubular design. The inner tube forms liquid internal heat exchanger (IHE) with an annular reaction chamber between IHE and outer wall. Temperature sensors are installed on the outer wall of reactor. The reaction chamber is filled with a metal hydride powder with average particle size of 10 μm and has inlet and outlet tubes at the ends, so gas can flow through the bed. Reactor is filled with LaNi₄.₈Mn₀.₃Fe₀.₁ alloy in amount of 1 kg [17]. The RSP-8(I) is mainly used for experiments because it allows to measure and control temperature at different zones of metal hydride bed.
The experiments are carried out in the following way: a prepared gas mixture of hydrogen and carbon dioxide modeling is fed to the inlet valve V4 of the RSP-8(I) reactor at a constant flow rate $j_0$ and pressure $P_{in}$. Gas mixture is filtered through hydrogen-absorbing material bed and is ejected through the outlet valve V5 at a limited flow rate lower than $j_0$. The metal hydride bed, cooled by the heat exchange liquid, absorbs hydrogen from gas mixture. The internal heat exchanger of the reactor is filled by silicon oil CAS: 63148-62-9, flow rate $g = 22$ L/min, temperature $T = 20 \, ^{\circ}C$. The hydrogen passed through the outlet valve is controlled by the gas analyzer 4. Temperatures of metal hydride bed and heat exchange liquid are measured by platinum thermal sensors.

2. Experimental results

Results of $H_2+CO_2$ gas mixture separation through $\text{LaNi}_{4.8}\text{Mn}_{0.3}\text{Fe}_{0.1}$ metal hydride bed with and without heat exchange liquid in the reactor are presented in Figures 2–4, $P_{in} = 0.55$ MPa.

A number of purification cycles with different operational parameters are performed in RSP-8(I) metal hydride reactor. Gas mixture consisted of 52% of $H_2$ and 48% of $CO_2$ prepared by partial pressures technique based on Dalton's law. Hydrogen recovery during the purification process is determined by the following equation:

$$\eta = 1 - \frac{V_{out}}{V_{in}},$$

where, $V_{out}$ is the volume of hydrogen in purged stream, $V_{in}$ is the volume of hydrogen in feed stream.

![Figure 2](image-url)  
**Figure 2.** Recovery ratio and absorbed volume of hydrogen: 1 – with reactor cooling, 2 - without cooling.

The temperature profiles of the metal hydride bed (Figure 3 and 4 left pictures) have a pronounced maximum, which corresponds to a drastic drop of recovery ratio during the purification process (Figure 3 and 4 right pictures). Due to the low effective thermal conductivity of the metal hydride bed, the heat dissipation during the sorption process is difficult. In the absence of cooling the temperature of metal hydride bed reaches 53-58 °C throughout the reactor at the initial stage of charge and practically stays unchanged during the sorption process. The significant temperature rise leads to the change of absorption equilibrium pressure of the alloy, which becomes closer to the inlet pressure causing a heat transfer crisis and terminating the sorption process [18]. Crisis phenomena lead to the decrease in the intensity of heat transfer and hydrogen absorption rate. As a result, hydrogen breaks through the metal hydride bed ($H_2$ concentration in the outlet gas from the reactor sharply increases), hydrogen losses during purification increase and the efficiency of metal-hydride flow-through reactors decreases dramatically (Figure 5, right pictures). For the case with cooling, temperature peaks are lower not exceeding 49°C and temperature decreases rapidly. If we take intersection point of recovery ratio and $H_2$ concentration at outlet as set point for cutoff, metal hydride bed with cooling can effectively utilize 70% of its hydrogen capacity, whereas without cooling it utilizes just 20% of capacity.
Recovery ratios at different initial parameters such as gas mixture composition, inlet flow rate and inlet pressure are shown in Figure 5.

In non-crisis modes, it is possible to achieve hydrogen recovery ratio up to 85% at different inlet flow rates and gas compositions, and utilize over 80% of hydrogen capacity of metal hydride bed (lines 1-3 in Figure 5 left). The change of inlet flow rate and gas mixture composition slightly affects the hydrogen recovery ratio. Change of inlet pressure has a stronger influence on the recovery ratio. The increase of the inlet pressure of the mixture $P_{in}$ from 0.5 to 0.8 MPa increases hydrogen recovery ratio by 8%, which is explained by the increase of the pressure drop driving hydrogen sorption at metal hydride bed being warmed up by the heat of sorption reaction (Figure 5). For the case without cooling, a decrease of recovery ratio is quite noticeable (17-26%), which is also connected with the presence of crisis phenomena. Therefore, selection of metal hydride composition with appropriate equilibrium pressure at operating temperatures and inlet gas mixture pressure is crucial because these parameters directly affect the efficiency of the flow-through hydrogen purification metal hydride system. The flow through metal hydride reactors for hydrogen separation can be applied to separation of H$_2$/CO$_2$ mixtures with low hydrogen content. The process is more cost efficient than, for example, PSA or membrane techniques. The capacity of metal hydride purification system can be easily increased by installation of additional metal hydride reactors without significant loss of kinetics.
Figure 5. Recovery ratios for H₂/CO₂ mixture at different initial parameters. At the left: 1 – 59%H₂ at $j_0 = 20 \text{ st.L/min}$; 2 – 55%H₂ at $j_0 = 3 \text{ st.L/min}$; 3 – 41%H₂ at $j_0 = 10 \text{ st.L/min}$; 4 – 52%H₂ at $j_0 = 3 \text{ st.L/min}$ without cooling; 5 – 27% H₂ at $j_0 = 3 \text{ st.L/min}$ without cooling. At the right: effect of inlet pressure for 27% H₂.

3. Conclusion
The separation of hydrogen-carbon dioxide gas mixtures with composition close to ‘biohydrogen’ was performed by AB₃ alloy containing RSP-8(I) metal hydride reactor. Hydrogen extraction was studied at different initial operation conditions. Cooling of metal hydride bed is a crucial factor for effective hydrogen purification. Metal hydride bed with cooling can effectively utilize 70% of its hydrogen capacity, whereas without cooling it utilizes just 20% of capacity at hydrogen recovery ratio over 85%. The increase of the inlet pressure of the mixture from 0.5 to 0.8 MPa increases the hydrogen recovery ratio by 8%. Metal hydride purification method can be a suitable solution for hydrogen extraction from different low hydrogen containing gas mixtures. However, further investigations of metal hydride compositions, as well as improvement of heat transfer in reaction bed are needed.

Acknowledgements
The work has been funded by the Russian Science Foundation (Project No. 17-79-20413).

References
[1] Levin D B, Pitt L and Love M 2004 *Int. J. Hydrogen Energ.* 29 173-85
[2] Show K Y, Lee D J, Tay J H, Lin C Y and Chang J S 2012 *Int. J. Hydrogen Energ.* 37 15616-31
[3] Debabrata D and Veziroglu T N 2008 *Int. J. Hydrogen Energ.* 33 6046-57
[4] Shihai G, Guoqing W, Dongliang Z, Yanghuan Z and Xinlin W 2011 *Rare Metal Mat. Eng.* 40 189-94
[5] Miura S, Fujisawa A, Tomekawa S, Taniguchi Y, Hanada N and Ishida M 2013 *J. Alloy Compd.* 580 (Sup. 1) S414-S7
[6] Saitou T and Sugiyama K 1995 *J. Alloy Compd.* 231 865-70
[7] Peterson J C and DiMartino S P 1987 *Metal hydride adsorption process for hydrogen purification*
U.S. Pat. 4,696,806
[8] Mordkovich V Z, Baichtock Y K, Dudakova N V, Korostyshhevsky N N and Sosna M H 1993 *Int. J. Hydrogen Energ.* 18 839-42
[9] Verbetsky V N, Malysheenko S P, Mitrokhin S V, Solovei V V and Shmaľko Y F 1998 *Int. J. Hydrogen Energ.* 23 1165-77
[10] Barbir F 2005 *PEM fuel cells: theory and practice*, Academic Press, Burlington, MA, USA
[11] Carrette L, Friedrich K A and Stimming U 2001 *Fuel Cells* 1 5-39
[12] Malysheenko S P and Romanov I A 2014 *High Temp+* 52 403-10
[13] Artemov V I, Lazarev D O, Yan'kov G G, Borzenko V I, Dunikov D O and Malysheenko S P 2004
High Temp+ 42 987-95
[14] Dunikov D O, Borzenko V I, Malyschenko S P, Blinov D V and Kazakov A N 2013 Therm. Eng+ 60 202-11
[15] Blinov D V, Dunikov D O, Kazakov A N and Romanov I A 2017 J. Phys. Conf. Ser. 891 012119
[16] Artemov V I, Minko K B and Yan’kov G G 2016 Int. J. Hydrogen Energ. 41 9762-8
[17] Malyschenko S P and Romanov I A 2014 High Temp+ 52 403-10
[18] Borzenko V, Dunikov D and Malyschenko S 2011 High Temp+ 49 249-56