

TECHNOLOGIES FOR HYDROGEN PRODUCTION BASED ON DIRECT CONTACT OF GASEOUS HYDROCARBONS AND EVAPORATED WATER WITH MOLTEN PB OR PB-BI

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ABSTRACT

Results of research aimed at the justification of advanced energy-saving and safe technology of low-cost hydrogen generation have been presented. The technology basis is direct mixing of water and/or gaseous hydrocarbons with Pb or Pb-Bi heavy liquid metal coolants. Its possible applications include the development of small-size hydrogen sources.

Keywords: hydrogen, lead, lead-bismuth, direct contact, water, hydrocarbons

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1. Introduction

The global energy crisis can be overcome through a change from the fossil fuel contaminating the environment, related costs rapidly rising, to pollution-free energy sources, primarily, hydrogen fuel. The problem of producing small amounts of hydrogen on site where necessary at the moment (small-size hydrogen sources), for example, for the fuel cells, has acquired special importance.

The long-term experience of IPPE gained with studies on heavy liquid metal coolants (HLMC) technology for NPP [2, 3] (as well as developments of Tokyo Institute of Technology [4]) suggest the feasibility of developing a technology based on direct mixing of HLMC with hydrogen-containing gases (steam, natural gas, etc.) to be safe and relatively simple in terms of facility design [1, 5-7]. There is every reason to believe that it will provide advantages owing to the following features: a) hydrogen-containing substances are heated up by their direct contact with HLMC (which means a significant simplification of heat exchanger design, cost reduction, and an increased efficiency because of separating wall elimination), and b) HLMC is used not only for heat removal but also to increase efficiency of thermal conversion of hydrogen-containing substances by the application of innovative processes of metal-gas chemical interaction.

2. Possible technologies of conversion of gaseous substances

There is a possibility to create small-size hydrogen sources based on the following processes: pyrolysis of hydrocarbons, steam decomposition and oxidizing conversion of hydrocarbons (by steam or oxides). Let us consider them more in detail.

2.1. Pyrolysis of hydrocarbons in HLMC

Pyrolysis of hydrocarbons ($t \geq 500^\circ\text{C}$) is the following chemical reaction (with methane as an example):



Figure 1 shows schematic diagram of possible implementation of this technology. Methane is supplied to the lower section of the reaction vessel filled with HLMC. Methane bubbles are heated up when passing through the HLMC layer, and partial methane decomposition proceeds according to expression (1). Additional decomposition of methane takes place in the free space [OR OUTAGE – в пезервьяпе] of the reaction vessel, streams of coolant heated up to the specified temperature flowing

continuously therein. At the outlet of the reaction vessel, there is a special device for separation of solid phase dispersed carbon from gas phase.

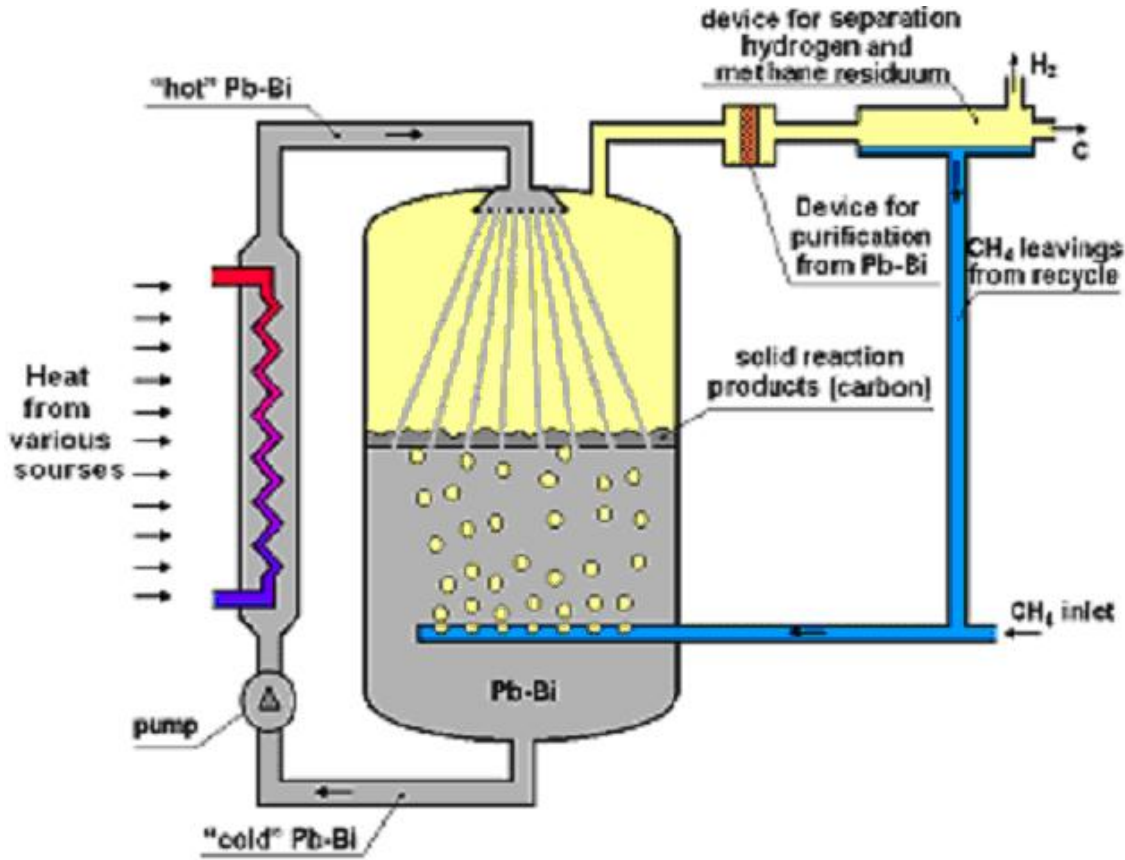


Figure 1. Schematic diagram of facility for hydrogen production from hydrocarbons.

2.2. Steam decomposition in HLMC

The following reaction characterizes steam decomposition ($t = 400-1000^\circ\text{C}$):



where [O] –oxygen dissolved in the liquid metal.

Possible design of facility for realization of this process is shown in Fig.2. Steam enters the lower section of the reaction vessel with HLMC. This causes appearance of air-lift effect intensifying heat transfer in HLMC. Generated hydrogen is easily separated from water in the condenser. In order to intensify hydrogen generation, oxygen dissolved in the liquid metal should be removed continuously from the reaction area. This can be achieved by special oxygen pump based on the use of ceramics made of solid oxide electrolyte with ion oxygen permeability. Voltage is applied to the pump electrodes to remove oxygen from HLMC.

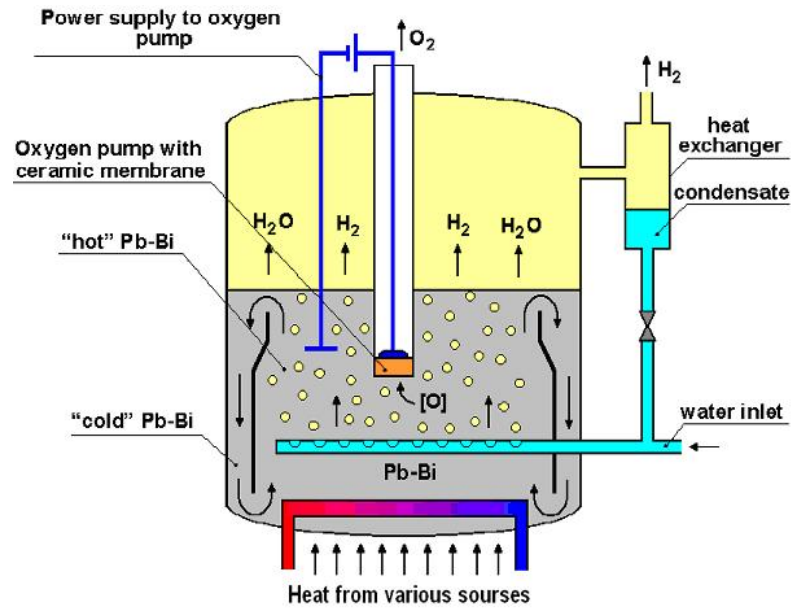


Figure 2. Proposed facility for water decomposition in HLMC.

2.3. Steam conversion of hydrocarbons in HLMC

Reaction of oxidizing (by steam) conversion of hydrocarbons ($\geq 500^\circ\text{C}$) is described by the following expression:



Possible version of facility for this technology is presented in Fig.3. The H_2 and CO_2 thus produced can be separated using various methods, for instance, by cooling down the mixture below CO_2 condensation temperature.

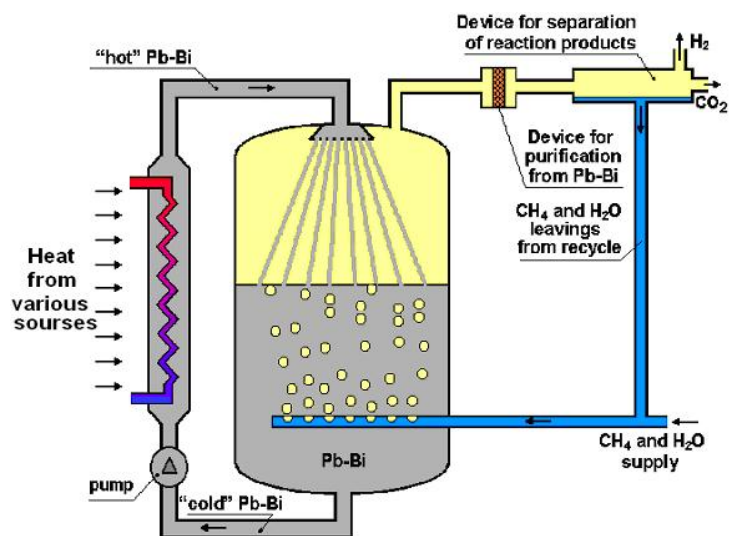
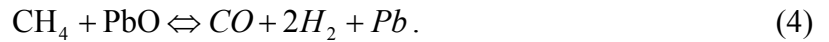


Figure 3. Design of facility for hydrogen generation by steam conversion of hydrocarbons.

2.4. Oxidation conversion of hydrocarbons in HLMC

The following reaction is possible in the case of oxidizing (by oxides) conversion of hydrocarbons (at $t \geq 500^\circ\text{C}$):



Design of facility for this process is shown in Fig.4.

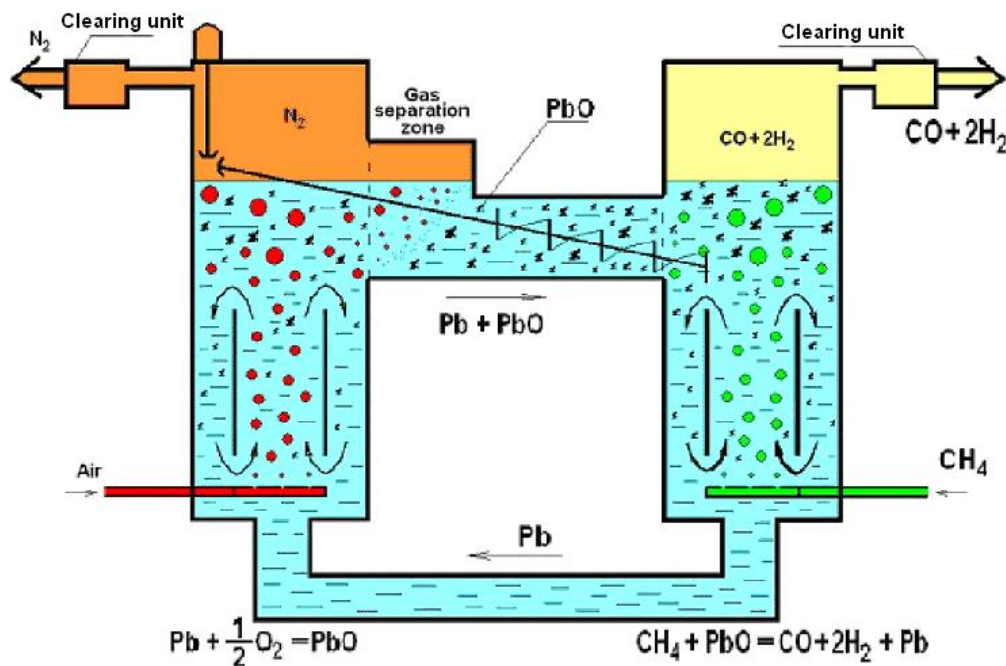


Figure 4. Facility for hydrogen production on the basis of oxide conversion of hydrocarbons.

The oxide conversion is more effective as compared to traditional steam conversion. The conversion effectiveness is increased owing to the use of innovative processes, such as oxidation of hydrocarbons by the oxides present in the reaction area as solid and/or liquid (dissolved in the liquid metal) substances. Continuous production of PbO is possible in the circuit when oxidizing HLMC by the atmospheric oxygen:



This reaction is characterized by heat generation. Therefore, PbO generator does not need continuous heating. A simple process of separation of the main air components, i.e., oxygen and nitrogen, is an important advantage when the coolant oxides are used.

In all above technologies, any heat source available can be used for heating HLMC.

3. Theoretical justification of hydrogen production reactions in HLMC

3.1. HLMC interaction with steam

All calculations are presented only for Pb-Bi coolant (they will be similar for lead).

As numerous research works have shown, the dependence of equilibrium oxygen activity in liquid Pb-Bi on temperature and a ratio of partial pressures of steam and hydrogen is determined by equation:

$$\lg a = \lg \frac{P_{H_2O}}{P_{H_2}} - 2,06 \cdot \frac{10^3}{T} - 2,13. \quad (6)$$

After transformations simple enough (6) we obtain the dependence determining the hydrogen fraction in equilibrium mix «H₂ – H₂O»:

$$\frac{P_{H_2}}{P_{H_2} + P_{H_2O}} = \frac{1}{1 + a \cdot 10^{2,06 \cdot \frac{10^3}{T} + 2,13}}. \quad (7)$$

The graphic representation of the hydrogen fraction in the equilibrium gas mix dependence on the oxygen activity and temperature is shown in Fig. 5.

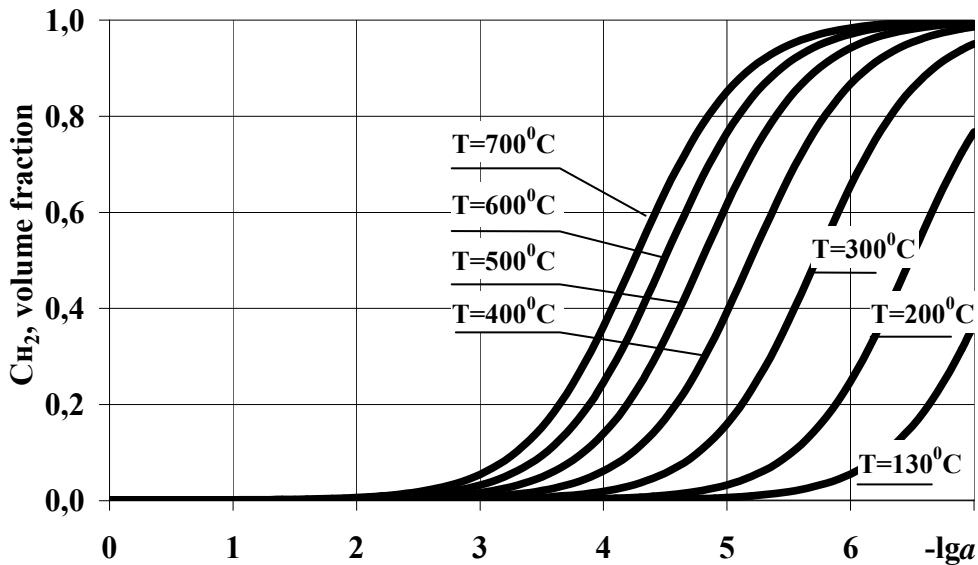


Figure 5. Dependence of hydrogen fraction in equilibrium mix on the oxygen activity and temperature.

Taking into account the data of (7) and diagram in Fig. 5, it becomes obvious that in all the temperature range studied, almost complete decomposition of steam (with formation of hydrogen) is theoretically possible. For maintaining the efficiency of decomposition of water steam it is necessary to ensure the minimum possible content of dissolved chemically active oxygen in liquid melt.

3.2. Interaction of HLMC with mixtures of hydrocarbon and various oxidizing agents

Results of calculations in terms of feasibility of hydrogen production in the interaction of gas hydrocarbons with various oxidizers in liquid HLMC are given in Table 1. The equilibrium constant values K_e^0 depending on temperature for various reactions are presented. Actually, the reaction can proceed in a direct pattern at $K_e^0 > 1$.

Table 1. Thermodynamics of possible decomposition reactions and methane conversion.

Reaction		Temperature, K				
		500	600	700	800	900
$\text{CH}_4 = \text{C} + 2\text{H}_2$	K_p^o	$4,0 \cdot 10^{-4}$	$1,0 \cdot 10^{-2}$	$1,2 \cdot 10^{-1}$	$7,3 \cdot 10^{-1}$	$3,6 \cdot 10^0$
$\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$	K_p^o	$1,1 \cdot 10^{-8}$	$1,3 \cdot 10^{-5}$	$2,4 \cdot 10^{-3}$	$1,2 \cdot 10^{-1}$	2,8
$\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$	K_p^o	$8,6 \cdot 10^{-11}$	$5,0 \cdot 10^{-7}$	$2,6 \cdot 10^{-4}$	$3,1 \cdot 10^{-2}$	1,3
$\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$	K_p^o	$6,6 \cdot 10^{-13}$	$1,9 \cdot 10^{-8}$	$2,9 \cdot 10^{-5}$	$7,7 \cdot 10^{-3}$	$5,9 \cdot 10^{-1}$
$2\text{CH}_4 + \text{H}_2\text{O} + \text{CO}_2 = 3\text{CO} + 5\text{H}_2$	K_p^o	$5,7 \cdot 10^{-23}$	$9,3 \cdot 10^{-15}$	$7,9 \cdot 10^{-9}$	$1,7 \cdot 10^{-4}$	$7,6 \cdot 10^{-1}$
$\text{CH}_4 + 2\text{PbO} = \text{CO}_2 + 2\text{H}_2 + 2\text{Pb}$	K_p^o	$3,2 \cdot 10^2$	$4,2 \cdot 10^4$	$1,6 \cdot 10^6$	$2,2 \cdot 10^7$	$2,2 \cdot 10^8$
$\text{CH}_4 + \text{PbO} = \text{CO} + 2\text{H}_2 + \text{Pb}$	K_p^o	$1,4 \cdot 10^{-5}$	$2,8 \cdot 10^{-2}$	$6,8 \cdot 10^0$	$4,4 \cdot 10^2$	$1,4 \cdot 10^4$

The analysis of Table 1 shows that reactions of thermal decomposition and oxidizing conversion of gas hydrocarbons at their contact with liquid melt of Pb-Bi are possible. And, as two bottom lines of the Table show, they can proceed effectively and at lower temperatures, compared to the reactions used in traditional technologies (see the 1-5 lines of the Table).

4. Experimental research of hydrogen production processes

4.1 Decomposition of water in HLMC

We have carried out the first studies [8] on hydrogen production in steam decomposition in liquid Pb-Bi. Oxygen from melt was transferred into a capsule from solid oxide electrolyte through which the electric current was passed. The results obtained are presented in Table 2.

Table 2. Results of hydrogen production in water decomposition in liquid Pb-Bi.

t, °C	Water flow rate, ml/h	Oxygen activity	Calculated value C_{H_2} , %	C_{H_2} , % (experimental value)
385	140	$2,7 \cdot 10^{-3}$	0,21	0,02
525	130	$4,1 \cdot 10^{-3}$	0,47	0,04
655	140	$8,5 \cdot 10^{-4}$	5,08	0,82
810	133	$\sim 1 \cdot 10^{-4}$	48,17	15,21

Relatively small concentrations of the received hydrogen are explained by the use of a low-efficiency oxygen pump. It is obvious that with this method hydrogen production would be justified at enhanced temperatures ($t > 800^\circ\text{C}$). Besides, it is clear that owing to the use of high temperatures the given method of hydrogen production will be more economic than the ordinary low-temperature electrolysis.

4.2 Steam conversion of propane in HLMC

Authors have carried out another series of investigations to show the principal possibility of hydrogen production by reaction (3). In this case propane was used as a modeling gas. The results obtained are shown in Table 3.

Table 3. Experimental results of steam conversion of propane in liquid Pb-Bi.

t, °C	$P_{H_2O}/P_{C_3H_8}$	Oxygen activity	C_{H_2} , % (experiment)
657	0,03	$2,78 \cdot 10^{-6}$	7,39
	0,65	$3,55 \cdot 10^{-5}$	8,23
	3,89	$9,41 \cdot 10^{-5}$	8,24
665	0,03	$3,38 \cdot 10^{-6}$	7,65
	0,18	$9,51 \cdot 10^{-6}$	8,15
	0,78	$3,65 \cdot 10^{-5}$	8,35
676	0,05	$4,45 \cdot 10^{-6}$	7,82
	0,26	$1,92 \cdot 10^{-5}$	8,42
	0,83	$6,02 \cdot 10^{-5}$	8,09
	1,73	$1,03 \cdot 10^{-4}$	8,60

The results presented in Table 3 have confirmed the feasibility of steam conversion of hydrocarbons in HLMC. Also they have indirectly confirmed the prospects of organization of conversion of hydrocarbons used as an oxidizer lead oxide (reaction 4), which can be present in liquid HLMC in suspended or dissolved form.

5. Conclusions

The concept of advanced energy-effective and safe technology of hydrogen production in small-size facilities has been proposed. The theoretical analysis as a justification of feasibility of hydrogen production in all processes covered has been carried out. The first experimental results have confirmed a principal possibility of hydrogen production in reactions of decomposition of water and steam conversion of propane in liquid HLMC. In case of successful realization of additional studies for the substantiation of the technology reported, it is possible to achieve a significant reduction of produced hydrogen cost, as well as that of the «hydrogen source-fuel cell» complex as a whole.

6. References

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