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PECULIARITIES OF HYDROGEN PRODUCTION TECHNOLOGY USING ENERGY STORAGE MATERIALS

The paper presents information about the possibility to produce high-purity hydrogen on a pilot and pilot-industrial scale (1000 m^3 H$_2$/hour) using energy storage materials and gives some peculiarities of this technology.

Keywords:energy storage materials, hydrogen, productivity, reactor, and carbothermic reduction.

Many researchers and economists believe the global crude oil, natural gas, and uranium ore reserves will be exhausted in 40, 70, and 100 years, respectively. Hydrogen is an alternative to the hydrocarbon fuel, with water having a chance to become an inexhaustible source for obtaining it. The world hydrogen output is steadily growing and has come to 72 million TPA (1995); 83 million TPA (2000); 95 million TPA (2005); and 107 million TPA (2010). In the 21st century, the hydrogen consumption is expected to reach many hundred millions TPA. Today, 10 techniques for hydrogen production have been known. Their detailed description is given in [1, 2]. The most widespread techniques for production of hydrogen from hydrocarbons (natural gas, oil, and coal) are those based on vapor-phase conversion. Theoretically, in order to get 1 tone of hydrogen by the vapor-phase conversion of natural gas one needs 2.5 tons of methane. Practically, the consumption is 4.5 tons. Therefore, natural gas used for hydrogen production cannot meet demand for hydrogen as energy material. Currently, 96% of hydrogen is produced from hydrocarbons (85% from natural gas, 11% from oil, coal, and other hydrocarbons, and 4% by water electrolysis). Out of $465 \cdot 10^9$ kJ/h energy consumed globally 7.2% ($33.38 \cdot 10^9$ kJ/h) belongs to hydropower stations, 5.4% ($25.11 \cdot 10^9$ kJ/h) accounts for nuclear power plants, 23.2% ($107.88 \cdot 10^9$ kJ/h) for natural gas, 34.8% ($161.82 \cdot 10^9$ kJ/h) for oil, and 29.4% ($136.71 \cdot 10^9$ kJ/h) for coal [2, 3].

The concept of new field of knowledge and science, hydrogen power engineering (or *hydrogen economy*), arose soon after the first world power crisis of 1975—1976. Hydrogen power engineering is assumed to always have raw material, water that is permanently available on the Earth. The mass of hydrosphere totals $1,664 \cdot 10^{18}$ g, that of the Earth is $5.9763 \cdot 10^{21}$ tons [3].

Heat of hydrogen H_2 and methane (CH_4) combustion is $Q_{H_2} = 142.97 \cdot 10^3$ and $Q_{CH_4} = 55 \cdot 10^3$ kJ/kg, respectively. Heat of combustion of oxygen mix is 15899.2 kJ/kg for hydrogen and 8619.04 kJ/kg for methane. Here, the advantages of hydrogen are obvious: high energy output ratio and availability of water.

The product of hydrogen oxidation is water:

$$2H_2 + O_2 = 2H_2O. \qquad (1)$$

So, hydrogen is environment friendly fuel for combustion engines that now consume hydrocarbon fuel.

The disadvantages of hydrogen as fuel as follows:

1) explosiveness of hydrogen mixed with oxygen (natural gas mixed with oxygen as well);

2) the need to store hydrogen in special underground storage or special gas holders (like natural gas);

3) the need to carefully monitor the integrity of hydrogen tanks using hydrogen sensors with an alarm.

COST AND OUTPUT OF HYDROGEN OBTAINED IN PRODUCTION CYCLE USING PROTOTYPE FACILITY AND ENERGY STORAGE MATERIALS

The capacity of facility using energy storage materials (ESM) shall be at most 100 m^3H_2/h or 2400 m^3H_2/daily, 72000 m^3H_2/monthly or 876000 m^3H_2/annually.

The cost of hydrogen produced annually (876 000 m^3H_2) can be estimated on the basis of the world price for 1 m^3 hydrogen of 99.99% purity, USD 3.5. Hydrogen obtained using ESM is 99.999% pure. If hydrogen price is assumed USD 3.5 per m^3 and costs of hydrogen production make up 10% of total revenues, the economic factor is USD 2 759 400 annually, i.e.: 876 000 m^3H_2/annually × USD 3.5 = USD 3 066 000, 3 066 000 – 306 600 = USD 2 759 400 annually; if the facility's capacity is 1000 m^3/h (8 760 000 m^3H_2/annually), consequently, the economic affect is ~ USD 26 000 000 annually.

The facility's hardware (having a capacity of 10 m^3/h) using EMS for hydrogen production and power generation shall be completely computerized, i.e. provided with a system for supply of EMS and water to the reactor, temperature control, control of hydrogen pressure inside the reactor, sensors for continuous automatic feed of reagents, and with pressure sensors of vapor-hydrogen mix fed to steam-hydrogen turbine to generate power for the consumers and for its own needs.

COST OF RAW ESM WITH PRE-PRODUCTION CHARGE INCLUDED

The quantity of aluminum consumed is estimated as:

$$2Al + 4H_2O = 2AlOOH = 3H_2\uparrow. \qquad (2)$$

To produce 100 m^3 hydrogen one needs 87.8 kg activated Al* (containing 81.7 pure Al); for the production of 1000 m^3 hydrogen 878 kg activated Al* is required. In 2015, the price for 99.7% Al was USD 1450 per ton, so 817 kg cost USD 1185. The cost of 30 kg activator is USD 300 and that of 40 kg modifier is USD 26; hence, the total cost of activated aluminum is USD 1511 per ton (at the initial stage).

The preparation of ESM is made in the granulating furnace with homogenous ESM alloy obtained. Using the dispenser ESM is continuously fed to the reactor where the reaction (2) runs with the formation of steam-hydrogen mix (H^2 + + H_2O_{vapor}) at 325 °C and at a total pressure of 14.0 MPa and boehmite (AlOOH). Boehmite can be considered waste to be regenerated using the carbothermal method:

$$2AlOOH \rightarrow Al_2O_3 + H_2O + + Me_{act} + Me_{modified}, \qquad (3)$$

$$2Al_2O_3 + 3C \rightarrow 4Al + Me_{act} + + Me_{modified} + CO_2 \qquad (4)$$

with the formation of initial aluminum alloy (ESM) and carbon dioxide.

Per each 1000 m^3 hydrogen produced 1785.7 kg boehmite is formed. For its reduction by the carbothermal method according to the equation (3) theoretically it is necessary to consume 267.86 kg 100 carbon. Let us assume that the moisture content in coal is 25%, and the ash content is the same, i.e. 25%. Consequently, the coal weight is 267.86 · 1.5 = 401.79 kg. The coal price is USD 100 per ton, therefore, 402 kg coal costs ~ USD 40.

OPERATING CHARACTERISTICS

Fig. 1 shows a flowchart of plant for hydrogen production. One can see that ESM arrives to the

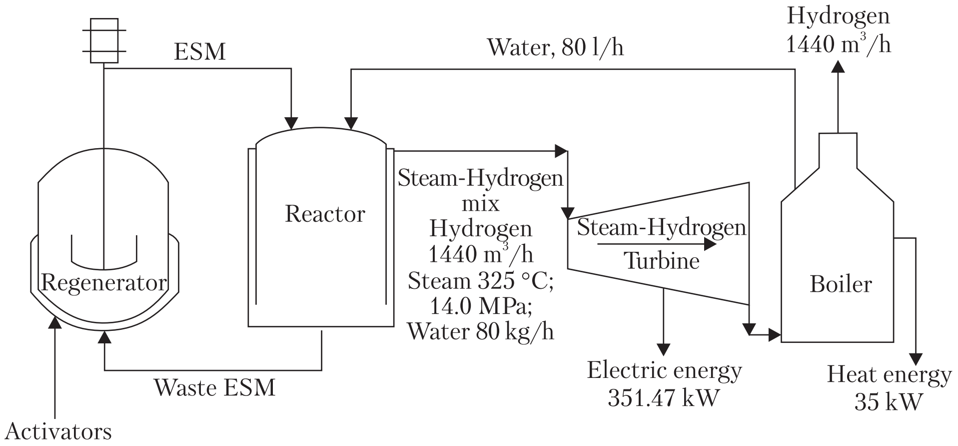

Fig. 1. Flowchart of the plant for hydrogen production using ESM

reactor and reacts with water to form steam-hydrogen mix at a rate 100 m^{3}H$_2$/h, at 325 °C and 200 atm. The mix is supplied to the turbine having a capacity of 351 kW. Daily, the turbine generates 8435 kW·h electric energy. The exhaust mix at a residual pressure of > 80 atm. comes to the boiler for condensation of water and its supply to the reactor.

The exhaust ESM is fed to the regeneration shop consisting of a set of departments such as the department for centrifugation of wet aluminum oxides and their drying, the department for their further baking up to Al_2O_3 at t > 300 °C, the regenerator (high-temperature electric furnace for carbothermal reduction of Al_2O_3) and the department for ESM granulation.

The scheme of electric furnace for carbothermal reduction of aluminum oxide with induction heating *4* and graphite electrodes *9* is given in Fig. 2. Obtained ESM aggregates are supplied to the reactor (see Fig. 1) using dispenser *12* and box *13* from high-pressure chamber with the help of special screw-type feeder.

Advantage of this method is ensured by the fact that using ESM in closed-loop cycle as working body oxidizing it when obtaining hydrogen from water and then reducing by carbothermal method the oxidation products it is not necessary to use such expensive and almost exhausted raw material as natural gas and petrol. Aluminum is widely spread worldwide and ranked the forth falling behind iron.

SOME PROBLEMS OF DESIGNING THE PLANTS FOR HYDROGEN GENERATION FROM WATER USING ESM

While designing the plants there are some problems to be further addressed for improving the plant performance.

Stage 1

1) To design a hydrogen plant prototype having a capacity of 10 m^{3}H$_2$/h (8.93 kg ESM/h), with ESM aggregates of given size (1—300 μm) obtained by spraying molten aluminum with metal activators; with production of ESM for operating the reactor in order to get hydrogen within 2—10 days, i.e. its continuous (uninterrupted) operation using computerized control and dispensers (this is necessary for making a conclusion on eligibility of equipment and applied technology);

2) To design an aggregate dispenser and a system for withdrawal of products of interaction of ESM and water (hydrogen and aluminum oxides — boehmite);

3) To design a boiler plant prototype for condensing water vapors with the formation of hydrogen and water;

4) To design a hydrogen-steam turbine having a capacity of 35 kW.

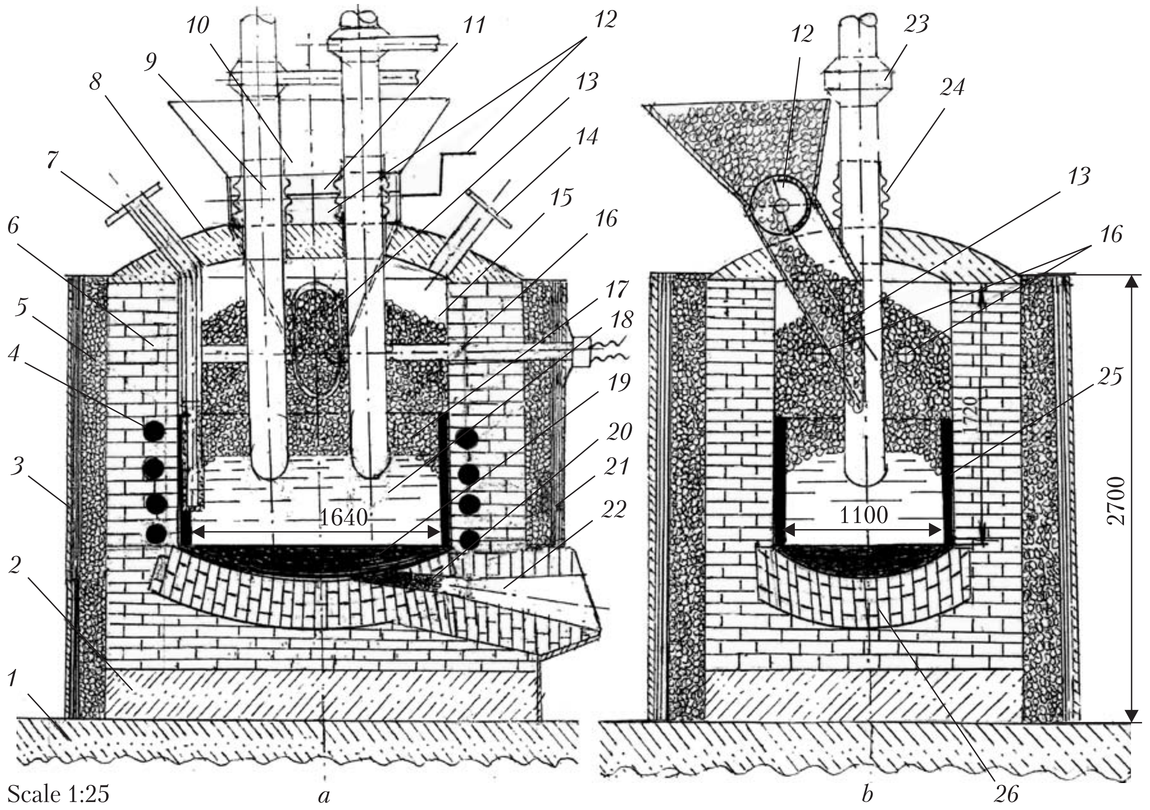

Fig. 2. Flowchart of ESM regenerator: *1* — furnace foundation; *2* — furnace bottom part; *3* — external case; *4* — heater; *5* — heating insulating filler; *6* — furnace lining; *7* — supply of inert gas; *8* — furnace cover; *9* — graphite electrodes; *10* — case of the filling chamber; *11* — hearth of the filling chamber; *12* — charging equipment, supplying node; *13* — distributor of the charging equipment; *14* — withdrawal of carbon dioxide; *15* — inner space of the furnace; *16* — thermocouple; *17* — coal and aluminum oxide mix; *18* — solution of coal and aluminum oxides; *19* — molten aluminum; *20* — tap hole for aluminum release; *21* — external insulator of the induction furnace; *22* — tap hole for reduced aluminum oxide; *23* — fixing of current feedthrough to the induction furnace; *24* — corrugated insulator of the induction furnace; *25* — heat insulator of the electric furnace; *26* — hearth lining

Stage 2.

1) To design prototype reactor having a capacity of 100 m^3H_2/h (ESM consumption rate is 89.3 kg/h) with aggregates having a size 1—300 μm from original aluminum and metal activators with continuous production of ESM before the start of ESM production in the regenerator. Time of operation of this reactor: 2—10 years in ESM-hydrogen closed-loop cycle;

2) To design a dispenser for this reactor and a facility for withdrawal of reaction products;

3) To design a facility for centrifugation of exhaust ESM;

4) To design furnaces for drying of exhaust products up to Al_2O_3;

5) To design a regenerator having a capacity of 89 kg ESM/h, with a working temperature up to 2200 °C (electric arc, induction or plasma heating) to reduce aluminum from Al_2O_3 (Fig. 2);

6) To design a steam turbine and an electric generator having a capacity of 350 kW;

7) To design a boiler plant prototype for condensing water vapors after the turbine, with the formation of low-wet hydrogen and water;

8) To design a plant for obtaining ESM aggregates of given size, 1—300 μm.

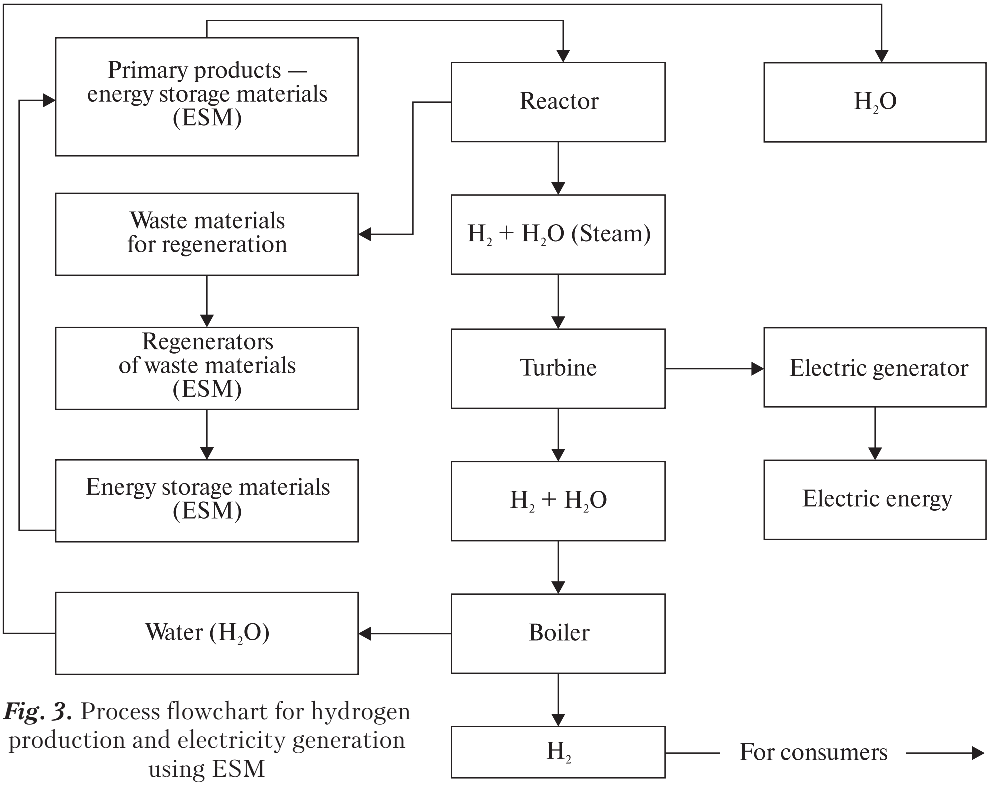

Fig. 3. Process flowchart for hydrogen production and electricity generation using ESM

The process flowchart of hydrogen production and power generation using ESM is showed in Fig. 3.

NECESSARY DATA FOR DESIGNING THE PLANTS OF SHOPS FOR PRODUCTION OF TRIAL AND COMMERCIAL HYDROGEN

To produce trial and commercial hydrogen the following equipment and facilities are required:

1) the reactors (2 units) for hydrogen production; they shall have a capacity of 100 m^3H_2/h (the 1st reactor), and 1000 m^3H_2/h (the 2nd one) and an ESM consumption rate of 80 kg/h and 800 kg/hour, respectively;

2) the regenerators (2 units) with a capacity to process 157 kg/h and 1570 kg/h Al_2O_3;

3) the turbines with 14 MPa pressure of steam-hydrogen mix (at 350 °C) and a capacity of 35 and 350 kW;

4) the power generators having a capacity of 35 and 350 kW;

5) the boilers for hydrogen production from steam-hydrogen mix after the reactor for hydrogen production having a capacity of 100 m^3H_2/h and 1000 m^3H_2/h;

6) the centrifuges for the separation of AlOOH (120 kg and 1200 kg, respectively) from water;

7) the electric furnaces for drying and baking AlOOH up to Al_2O_3 (157 kg/h and 1570 kg/h Al_2O_3);

It is necessary to analyze the possibility of designing gasholders (having a volume of 1000 m^3 and 10000 m^3) for storage of hydrogen at a pressure of 10 MPa.

Thermochemical principles of carbothermal reduction of Al_2O_3 at a temperature of up to 2200 °C

For the reaction

$$2Al_2O_3 + 3C = 4\ Al^* + 3CO_2 \qquad (5)$$

to get 157 kg and 1570 kg Al_2O_3 it is necessary to consume 27.8 kg and 278 kg coal, respectively;

taking into consideration the ash content and the moisture content (25—30%) this amount increases up to ~42 и 420 kg coal. The calorific capacity of 278 kg pure carbon is equal to 9116 MJ. The heat of formation of 1570 kg Al_2O_3 is 25 797.250 MJ:

$$\frac{Q_{Al_2O_3}}{Q_C} = 2.83, \qquad (6)$$

$$\Delta Q_C = 25\,797\,250 - 9\,116\,000 = \\ = 16\,681\,250 \text{ kJ}, \qquad (7),$$

that is equivalent to 4634 kW·h. This amount of electricity should be consumed by the regenerator's electric arc furnace to reduce 1570 kg Al_2O_3 to the metal state.

Requirements for the process area for industrial hydrogen production:

1) The floor area of the shop for hydrogen production depends on capacity of the plants and can range from 20 to 100 m², with auxiliary rooms (workshops, warehouses, etc.) occupying 200 m²;

2) the rooms where the hydrogen producing plants are installed shall be equipped with:

a) sensors of hydrogen concentration in air and acoustic alarm;

b) explosion resistant devices with specific alarm;

c) hood fans and vacuum ventilation;

d) tap water (1 m³/h) and fire extinguishing agents.

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ОСОБЛИВОСТІ ТЕХНОЛОГІЇ ОДЕРЖАННЯ ВОДНЮ З ВИКОРИСТАННЯМ ЕНЕРГОАКУМУЛЮЮЧИХ РЕЧОВИН

У статті наведено відомості про можливість одержання високочистого водню в дослідних та дослідно-промислових (1000 м³H_2/год.) масштабах з використанням енергоакумулюючих речовин і вказані деякі особливості даної технології.

Ключові слова: енергоакумулююча речовина, водень, продуктивність, реактор, карботермічне відновлення.

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ОСОБЕННОСТИ ТЕХНОЛОГИИ ПОЛУЧЕНИЯ ВОДОРОДА С ИСПОЛЬЗОВАНИЕМ ЭНЕРГОАККУМУЛИРУЮЩИХ ВЕЩЕСТВ

В статье приведены сведения о возможности получения высокочистого водорода в опытных и опытно-промышленных (1000 м³H_2/час) масштабах с использованием энергоаккумулирующих веществ и указаны некоторые особенности данной технологии.

Ключевые слова: энергоаккумулирующее вещество, водород, производительность, реактор, карботермическое восстановление.

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