Standalone hydrogen generator based on chemical decomposition of water by aluminum

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Abstract

A standalone hydrogen generator (SHG) has been developed based on chemical decomposition of water in heterogeneous compositions containing finely dispersed aluminum powder and crystallohydrates of sodium metasilicate. The kinetics of hydrogen generation has been studied depending on constants of the aluminum activation and oxidation rate, and aluminum and oxygen concentrations. In the hydrogen accumulation kinetics, the length of the induction period is determined by the concentration of oxygen. The SHG design, hydrogen selection and capacity are discussed. The availability and low cost of domestically manufactured chemical agents make the SHG a promising choice as the source of hydrogen for various applications, including nuclear power plants (NPP).

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Introduction

At the present time, a growingly increased attention is given to studies into the generation of hydrogen from the interaction of powders of metals and alloys, specifically aluminum, with water. A decisive role in the process is played by the properties of metal oxides forming a surface film. High chemical stability of aluminum to water and steam effects is explained by the presence of surface films of aluminum oxide (Al₂O₃). To make aluminum active in the interaction with water, it is required to remove the surface oxide film. A number of techniques are used to activate aluminum, including treatment by sodium hydroxide, high temperature, high pressure, and gallium-indium alloys, which are however ecologically hazardous, complex and expensive [1–5]. Russian-patented hydrogen production methods [9,10] have been developed based on studies into the kinetics and the mechanism of reactions in hydroreactive heterogeneous compositions containing aluminum and silicon or calcium-containing compounds as activators [6–8].

For practical applications, it is desired that hydrogen is produced at the consumption point, which reduces greatly the cost of storage and transportation, and makes it easier to use [2,11]. This is achieved through the use of standalone hydrogen generators. This paper presents a description of a standalone hydrogen generator (SHG) patented in the Russian Federation [12], considers the kinetics of hydrogen generation with regard for the formulation of heterogeneous compositions and the environment components, and highlights some of the issues involved in control of the SHG hydrogen generation process.

Experiment

The hydrogen generator consists of two metal chambers in the form of cylinders mated through a threaded joint with a rubber gasket (Fig. 1).

The lower reaction chamber (1) is filled with a heterogeneous composition (2); the upper chamber (3) with a metallic bottom (4) is filled with an aqueous solution of sodium metasilicate crystallohydrate (Na₂SiO₃·9H₂O) which acts as an aluminum activator; the aqueous activating solution is fed...
from the upper chamber into the lower chamber using a threaded solution feed regulator (7) representing a rod with a tapered tail-end that makes it possible to supply the required amount of aqueous solution at the preset rate (see Fig. 1). The aqueous activating solution is filled through the window (6) in the chamber cover. The rate of the aqueous solution supply from the upper chamber to the lower chamber is regulated by the pointer of segment numbers (12), the indication of which is applied to the upper chamber cover surface.
The hydrogen generated by the composition is let out of the lower chamber through a metal tube (8) which is connected, through the shell (9), to the flexible rubber tube (10) connected to the hydrogen receiver.

The SHG operates as follows. A heterogeneous composition containing aluminum in the form of finely divided powder and water (12) is filled in the lower reaction chamber (1). Chemically different water can be used (distilled, mineralized, wastewater). Through the filling window (6), the upper chamber (3) is filled with sodium metasilicate crystallohydrate (Na₂SiO₃•9H₂O) (5). The generator and hydrogen production are started by supplying a particular amount of the aqueous activating solution into the chamber (1), using the threaded solution feed regulator (7), at a particular rate (ml/min). The hydrogen generation rate, the hydrogen temperature, the generation time (min, h) and the hydrogen generator capacity (/h) are regulated by varying the formulation of the heterogeneous composition, the activator concentration in the aqueous solution and the rate of the solution feed into the reaction chamber (1). Specific to the generator operation is rapid startup with the working conditions achieved just in several minutes and the ease of the hydrogen generation rate control. The SHG operates without an external power source in an autonomous mode. It is environmentally friendly, portable, reliable and easy to operate.

The kinetics of the hydrogen generation using the SHG was studied on compositions containing aluminum powder (GOST 5494-95, grade PAP-2) with the particle dimensions of 25 to 50 μm, the particle thickness of 0.25 to 0.50 μm, and the surface area of 1.6 m²/g, and distilled water. The aqueous solution of sodium metasilicate crystallohydrate (Na₂SiO₃•9H₂O) is fed into the reaction chamber (1) at a preset rate using the threaded regulator. Reactions take place at a temperature of not more than 80 °C in a chamber with a volume of 500 ml. The SHG provides for a theoretically threshold yield of pure hydrogen (0.12 kg per 1 kg of aluminum) at a rate of 0.01 to 1.5 l/min with a capacity of 0.01 to 0.1 m³/h and a hydrogen generation time of 0.1 to 6 h. Gas chromatography method was used to determine the composition of the evolved gas (hydrogen content 98%, carbon dioxide content ~0.03%, carbon oxide content ~5·10⁻⁵%), that is, the SHG generates pure hydrogen with no impurities of greenhouse gas (CO₂) and carbon oxide (CO) that poison platinum and palladium catalysts of low-temperature fuel elements.

Results and discussion

Chemical processes in hydroreactive heterogeneous compositions containing aluminum powder and sodium metasilicate crystallohydrate (as the activator) take place in the presence of oxygen which is in the gas phase of the reaction vessel or is dissolved in water. So it is necessary to take into account the reaction of aluminum oxidation by oxygen. With this reaction taken into account, the processes taking place in the composition may be described using a simplified pattern as follows:

\[ \text{Al}_2\text{O}_3 + \text{activator} \rightarrow k_1[\text{Al}_{\text{act}} + \text{products}]. \] (1)

\[ 4\text{Al}_{\text{act}} + 3\text{O}_2 \rightarrow k_2[2\text{Al}_2\text{O}_3] \] (2)

\[ 2\text{Al}_{\text{act}} + 6\text{H}_2\text{O} \rightarrow k_3[2\text{Al(OH)}_3 + 3\text{H}_2]. \] (3)

The activator breaks down and removes the surface oxide film and brings aluminum into an activated state (Al₄act) with the rate constant k₁ (1). In the presence of atmospheric oxygen, the activated aluminum surface is oxidized with the rate constant k₂, and oxide is formed (Al₂O₃) (2). Simultaneously, water contained in the composition interacts, with the rate constant k₃, with the activated surface of aluminum with formation of hydrogen and aluminum hydroxide (Al(OH)_3) (3). The thickness of the aluminum oxide layer is much smaller than the aluminum particle thickness. Such initial state of the heterogeneous composition makes it possible to identify the nature of the hydrogen accumulation kinetics depending on the relation of the aluminum surface activation and oxidation rate constants.

The following system of differential equations can be used to describe the hydrogen accumulation process:

\[ \frac{d[S]}{dt} = -k_1 \cdot [S] + k_2 \cdot [A] \cdot [O_2], \] (4)

\[ \frac{d[A]}{dt} = k_1 \cdot [S] - k_2 \cdot [A] \cdot [O_2], \] (5)

\[ \frac{d[O_2]}{dt} = -k_2 \cdot [A] \cdot [O_2]. \] (6)

\[ \frac{d[H_2]}{dt} = k_3 \cdot [A], \] (7)

where [S] is the area of the initial aluminum surface; [A] is the area of the activated aluminum surface; [O₂] is the oxygen concentration; and [H₂] is the hydrogen concentration.

Since there is no analytical solution to this system of equations, it was solved numerically, using the Mathcad 14 package. When solving the system of equations, the relations of the reaction rate constants k₁ and k₂, the initial oxygen concentration, and the number and the surface area of aluminum particles were varied. It follows from an analysis of the obtained calculated kinetic curves that characterize the variations of the surface covered with aluminum oxide, and the activated aluminum surface that the hydrogen accumulation process depends heavily on relations in the system of the aluminum oxide and oxygen concentrations (Al₂O₃/O₂).

We shall consider the kinetics of the hydrogen accumulation process at a permanent ratio of the activation and oxidation rate constants, and with the constant oxygen quantity and aluminum quantity variation. Fig. 2 presents calculated kinetic curves of the hydrogen accumulation depending on time for compositions containing equal quantities of oxygen but different quantities of aluminum particles of a similar size. The initial kinetic curve segment exhibits the presence of a time interval during which no hydrogen is accumulated in the composition. This time interval should be identified as the induction period in the hydrogen accumulation process. We shall note that the induction period length decreases and
Fig. 2. Kinetic curves of hydrogen accumulation in oxygen-containing compositions versus the mass of aluminum: 1, 2 and 3 correspond to aluminum masses 5, 2 and 1 (rel. units).

Fig. 3. Kinetic curves of hydrogen accumulation versus the mass of aluminum in the absence of oxygen: 1, 2 and 3 correspond to aluminum masses 5, 2 and 1 (rel. units).

the hydrogen accumulation rate increases as the aluminum quantity in the composition increases.

Calculated kinetic curves of the hydrogen accumulation obtained for the case of no oxygen in the composition and different quantities of aluminum are compared in Fig. 3. It can be seen that there is no practically induction period on the kinetic curves and the hydrogen accumulation rate on the linear curve segment increases pro rata the aluminum mass. The comparison of the hydrogen accumulation curves in Figs. 2 and 3 shows that the hydrogen accumulation kinetics is
heavily affected by the presence of oxygen in the com-
positions, which manifests itself in the existence of a time span
during which no hydrogen is formed. Activated aluminum
disappears as the result of the surface oxidation and the alu-
minum oxide formation.

The induction period length increases proportionally to the
oxygen quantity, which can be seen from a comparison of the
kinetic curves depending on the oxygen quantity and an equal
aluminum mass (Fig. 4). The nature of the hydrogen evolu-
tion kinetics in the presence of oxygen depends greatly on
the ratio of the aluminum surface oxidation and activation
reaction rates: the induction period grows as the said ratio
increases (see Fig. 4). When the ratio of the activation and
oxidation rate constants is selected, one shall take into ac-
count that the constants of the rate of the oxygen addition to
aluminum are much higher than the aluminum activation rate
constants ($k_2 >> k_1$).

The initial stage of the aluminum activation was considered
above assuming that the quantity of oxygen in the compo-
sition is relatively small. When the concentration of oxygen in
the composition is high, a great quantity of aluminum ox-
ide is formed in the process which is commensurable with
the aluminum particle mass. In this case, as the result of a
multiply recurring cycle of the reactions of aluminum activa-
tion (Al$_2$O$_3$ removal) and the repeated formation of aluminum
oxide from the interaction with oxygen, the metal particle
size and mass decrease gradually which leads to its dispa-
rance in the composition and to the termination of the
hydrogen formation. As the result, as the linear segment of
the hydrogen accumulation curve ends, the accumulation rate
decreases and the total quantity of the hydrogen evolved re-
mains unchanged. This manifests itself on the kinetic curves
of the hydrogen accumulation in the linear segment being
followed by a stable segment with no hydrogen concentration
increase.

The calculated kinetics of the hydrogen accumulation in
heterogeneous compositions was compared with the exper-
imental results obtained in a study into the process of the SHG
hydrogen generation process. The major parameters that de-
termine the hydrogen generator operation are aluminum mass,
concentration of the activator in aqueous solution, rate of the
aqueous solution feed into the reaction volume, and water
quantity and temperature.

In an analysis of experimental data, one should take into
account that the volume of the chamber, in which the reaction
takes place, is 500 ml, and it contains about $3 \cdot 10^{21}$ molecules
of oxygen. As estimated, $1.4 \cdot 10^{19}$ molecules of oxygen will
be required to oxidize a surface of 1 g of aluminum powder
with the particle dimensions of 25 to 50 $\mu$m and a surface of
1.6 m$^2$/g, that is, the reactor contains enough oxygen to form
about 35 layers of aluminum oxide. This means that, along
with the reaction leading to the aluminum activation, an effec-
tive activated aluminum surface oxidation reaction takes place
in the composition. Since no hydrogen is generated during the
aluminum activation, then the activation–oxidation chain re-
action leads to a decrease in the hydrogen yield as compared
to the calculated value.

We shall consider the dependence of the liberated hydro-
gen amount on the aluminum mass with the predetermined
concentration of the activating solution prepared based on dis-
tilled water and on the constant rate of the solution supply
into the SHG reactor.
Fig. 5. Kinetic curves of hydrogen accumulation versus the mass of aluminum: 1, 2 and 3 correspond to 3, 6 and 7.5 g. The feed rate of a 20% aqueous solution of sodium metasilicate crystallohydrate is 2 ml/min.

Fig. 6. Kinetic curves of hydrogen accumulation versus the concentration of sodium metasilicate crystallohydrate in the aqueous solution: 1, 2 and 3 correspond to 20, 10 and 5%. The feed rate of a 20% aqueous solution of sodium metasilicate crystallohydrate is 2 ml/min.
It can be seen from Fig. 5 that the induction period of hydrogen accumulation increases with the aluminum mass decrease in accordance with the proposed theoretical model. When the aluminum mass is constant, the oxygen concentration variation effects on the hydrogen accumulation kinetics manifest themselves in a decreased rate of the surface oxidation, in a variation in the ratio of the oxidation and activation rates, and in prolongation of the induction period.

The dependence of the evolved hydrogen amount on the concentration of the activator in the aqueous solution with the preset aluminum mass and with the constant rate of the aqueous solution feed was studied on the SHG (Fig. 6). An induction period and a linear and the final hydrogen accumulation segments can be identified on the kinetic curves. Curve 1 corresponds to a 20% concentration of the activator in the solution at the solution feed rate of 2 ml/min and the aluminum mass of 7.5 g. The induction period is more pronounced on curve 2 corresponding to a 10% concentration of sodium metasilicate crystallohydrate than on curve 1. Curve 3 (a solution with 5% of sodium metasilicate crystallohydrate) characterizes the kinetics of the hydrogen accumulation only at the induction period phase. It is evident that the initiation reaction rate can be changed and the hydrogen generation rate can be controlled by varying the concentration of the activator in the solution.

Fig. 7 presents the dependence the evolved hydrogen amount on the feed rate of the aqueous activating solution. It can be seen that the rate of the hydrogen evolution is proportional to the solution feed rate. The total amount of hydrogen corresponds to the theoretical value. With the solution feed rate being 2 ml/min (curve 1) and 3 ml/min (curve 2), the dependence of the hydrogen yield on time is S-shaped. It is possible to change the length of the induction period and the time for which the threshold hydrogen yield is achieved by varying the activating solution feed rate.

**Conclusion**

The developed standalone hydrogen generator based on chemical decomposition of water in heterogeneous compositions containing finely divided powder of aluminum and sodium metasilicate crystallohydrates makes it possible to obtain a theoretically threshold yield of pure hydrogen. All domestically manufactured chemical ingredients are readily available and chemically safe and can be stored in normal conditions for a long time. Preliminary estimates show that the technical and economic parameters of the hydrogen production technology using aluminum, aqueous chemical activator solutions and the SHG are not worse than in other hydrogen production technologies.

The SHG-based production of hydrogen fuel offers a number of technological, economic, ecological and social advantages as compared to other hydrogen generation techniques when considering the level of the integration costs of implementing the whole of the hydrogen process chain: production, storage, transportation, distribution and end consumption. The SHG may be used at nuclear power plants as an available and rapidly deployable source for the supplier-independent production of hydrogen.

Broad availability and low cost of chemical agents make it possible to look upon SHGs as compact sources of hydrogen to be used for supplying telecommunication systems as well as by individual consumers outside centralized...
electricity supply systems, especially in remote and difficult-of-access localities.

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