

UDC 661.961.1

*V.V. Solovey<sup>a</sup>, M.M. Zipunnikov<sup>a</sup>, V.B. Poda<sup>b</sup>, I.O. Vorobjova<sup>a</sup>***HYDROGEN GENERATION FROM WATER BY USING ALLOYS BASED ON SILICON AND ALUMINIUM**<sup>a</sup> **A. Pidgorny Institute of Mechanical Engineering Problems of the National Academy of Sciences of Ukraine, Kharkiv, Ukraine**<sup>b</sup> **National Aerospace University named after N.E. Zhukovsky «Kharkiv Aviation Institute», Kharkiv, Ukraine**

We considered the process of hydrogen generation from water by using the alloys based on aluminium and silicon with the alloying additions of alkaline earth metals. The degree of completeness of the interaction between the above alloys and NaOH solution (10–13.3%) was determined for the range of initial temperatures of 90°C to 130°C. The required aluminium content in the ferro-silicon-aluminium alloys should be about 25–30% to intensify the hydrogen generation process in a laboratory reactor with a volume of  $1.13 \cdot 10^{-3} \text{ m}^3$ . The reactions of ferro-silicon and ferro-silicon-aluminium alloys with water were investigated in an AVG-45 autonomous balloon-type gas generator. The Gibbs energy value was calculated taking into account the influence of pressure changes in the gas generator. Recommendations have been developed to apply a silicone method of hydrogen generation in the hydrogen gas generators using aluminium-silicon alloys. The interaction of aluminium–sodium hydride composites with the NaH content of 23 wt.% and 50 wt.% as well as the samples of sodium aluminium hydride ( $\text{NaAlH}_4$ ) with water was studied to use them in the hydrogen gas generators. The procedure of hydrogen generation by means of hydro-reactive substances was adopted as a basic one to use in the hydrogen generation systems and in the developed system of hydrogen storage and hydrogen supply in experimental samples of the autonomous lifting installations.

**Keywords:** ferrosilicon, ferrosilicon-aluminium, hydrogen, water, aluminium hydride.**DOI:** 10.32434/0321-4095-2020-131-4-148-156**Introduction**

Expansion of the hydrogen application areas is associated with the qualitative changes currently taking place in the chemical, machine building, metallurgical and energy industries.

Ferrosilicon alloy FS 75 (Fe 20–25, Si 74–80, Al 0.6, Cr 0.5, P 0.05, and S 0.03) is used in a silicone method of hydrogen generation from water in weather stations and in aerostatics [1,2]. Silicon is an element that displaces hydrogen from water in the presence of caustic soda.

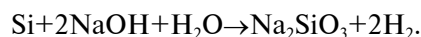
To date, the thermodynamics and kinetics of the interaction a caustic soda solution with different aluminium powders and aluminium activated by indium, gallium and tin have been investigated. As far as the silicon alloys is concerned, only some experiments were conducted with ferrosilicon FS 75 and ferrosilicon-aluminium alloys (FSA) obtained

by alloying of pure components [3,4].

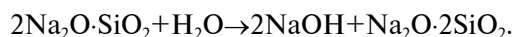
The aim of this work is to study the process of interaction of the alloys based on silicon and aluminium with water for hydrogen generation, in particular in autonomous lifting installations.

**Experimental, results and discussion**

The silicone method of hydrogen generation is described by the following equation [5]:



According to stoichiometry, it needs to take 80 g of caustic soda for every 28 g of silicon soda. In high-pressure gas generators, the consumption of caustic soda amount can be much smaller, since sodium silicates are formed:



As a result, free sodium hydroxide is released and sodium silicate is formed. Sodium silicate and its solutions are usually called soluble glass and liquid glass, respectively. The main characteristic of soluble glass is the number  $n$ , which shows how many silica molecules ( $\text{SiO}_2$ ) are related to one molecule of sodium oxide ( $\text{Na}_2\text{O}$ ). Sodium silicate with  $n=2$  can be further hydrolyzed to form silicates with a larger number  $n$ . Aqueous solutions of silicates can be generally represented by the formula  $\text{Na}_2\text{O} \cdot n\text{SiO}_2 \cdot m\text{H}_2\text{O}$ , where  $m$  is the number of water molecules that are the part of the silicates [6].

The study of the kinetics of hydrogen generation was performed in a laboratory reactor that provides an isochoric process ( $V=1.13 \cdot 10^{-3} \text{ m}^3$ ) (Fig. 1).

The hydrogen generating alloys have the following compositions (wt.%):

A-98CaMg – Al 98.4, Ca 0.8, and Mg 0.8;

AB 86 – Si 5.0, Al 84, Cu 4.0, Sn 0.2, Mg 3.0, Zn 3.5, and Pb 0.3;

FS 75 Ba1 – Fe 19.3, Si 78.4, Al 1.3, and Ba 1.0;

FS 75 Ba4 – Fe 18.1, Si 75.1, Al 2.0, and Ba 4.8;

FSA 15 – Fe 7, Si 78, and Al 15;

FSA 30 – Fe 10.3, Si 59.9, and Al 29.8;

FSA 30Mn1 – Fe 10, Si 56.83, Al 31.6, and Mn 1.57.

The results of the experiments are shown in Tables 1 and 2 and Figs. 2 and 3. The reaction was monitored by increasing the pressure in the reactor. The amount of the released gas was estimated by the gas meter.

The degree of conversion ( $\alpha_c$ ) was determined as the ratio of the maximum actually released

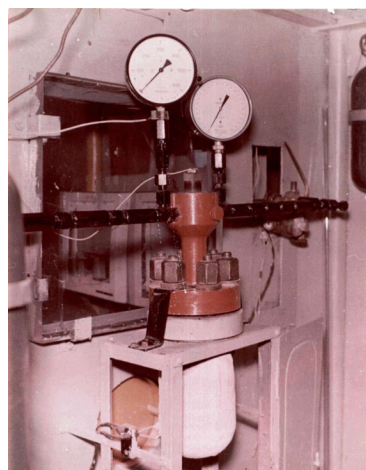


Fig. 1. Laboratory reactor with a volume of  $1.13 \cdot 10^{-3} \text{ m}^3$

hydrogen volume to the theoretically possible one:

$$\alpha_c = V_r / V_T,$$

where  $V_r$  is the volume of hydrogen that was released during the reaction and reduced to normal conditions; and  $V_T$  is the theoretical volume of hydrogen released by the interaction of  $m$  kg of pure element (Si or Al) with water.

For the silicon-aluminium alloys,  $V_T$  was determined by the rule of additivity for the all alloy active parts.

The rate of hydrogen evolution was calculated by the following formula

$$W = \frac{\Delta V}{m \Delta \tau},$$

where  $\Delta V$  is the volume of hydrogen released ( $\text{m}^3$ );  $\Delta \tau$  is the duration of hydrogen evolution (s); and  $m$  is the alloy weight (kg).

Table 1

**Dependence of the hydrogen evolution rate and the completeness of the reaction of FSA and FS alloys on sodium hydroxide concentration. The initial reaction temperature  $t=90^\circ\text{C}$ . The alloys weight  $m=5 \cdot 10^{-3} \text{ kg}$ . The particle diameter  $d=(0.5-1.5) \cdot 10^{-3} \text{ m}$**

Alloy type	Concentration of sodium hydroxide, wt.%	Maximal temperature, $t_{\text{max}}, ^\circ\text{C}$	Reaction time, $\tau \cdot 10^{-3}, \text{ s}$	Maximal reactions rate $W \cdot 10^3, \text{ m}^3/(\text{kg} \cdot \text{s})$	Reaction completeness, $\alpha$
FS 75 Ba 1	10	105	2.4	0.009	45
	13.3	104	1.5	0.16	60
FSA 30	10	91	4.92	0.42	28
	13.3	94	4.8	0.46	30
A-98CaMg	10	105	0.11	8.7	99
	13.3	107	0.1	8.8	99
AB 86	10	94	0.9	3.51	96.4
	13.3	96	0.85	3.53	98

Table 2

Dependence of the hydrogen evolution rate and completeness of the reaction of FSA and FS alloys on sodium hydroxide concentration. The initial reaction temperature  $t=90^{\circ}\text{C}$ . The alloys weight  $m=5\cdot 10^{-3}$  kg. The particle diameter  $d=(0.5-1.5)\cdot 10^{-3}$  m

Alloy type	Concentration of sodium hydroxide, wt.%	Maximal temperature, $t_{\text{max}}, ^{\circ}\text{C}$	Reaction time, $\tau\cdot 10^{-3}$ , s	Maximal reactions rate $W\cdot 10^3$ , $\text{m}^3/(\text{kg}\cdot\text{s})$	Reaction completeness, $\alpha$
FS 75 Ba 1	10	142	1.26	0.096	52
	13.3	135	1.23	0.95	70
FS 75 Ba 4	10	137	2.4	0.04	30
	13.3	133	0.37	0.5	36
FSA 15	10	131	2.6	0.14	51
	13.3	133	2.9	0.19	53
FSA 30	10	133	3.66	2.1	51
	13.3	135	1.68	3.9	63.6
FSA 30 Mn1	10	131	2.2	0.2	0.4
	13.3	132	2.08	0.16	0.43
A-98CaMg	10	132	0.13	7.8	99
	13.3	134	0.2	8.1	99
AB 86	10	136	1.2	2.7	99
	13.3	137	1.1	2.9	99

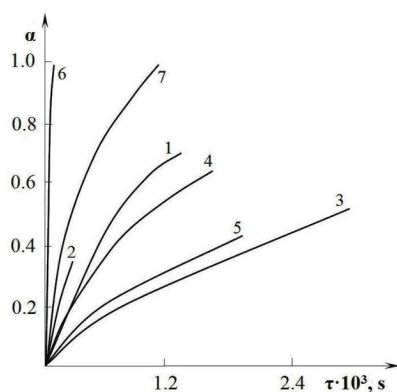


Fig. 2. Dependence of the reaction completeness on time.

The concentration of sodium hydroxide was 13.3%,  $T_{\text{init}}=130^{\circ}\text{C}$ . 1 – FS 75 Ba 1; 2 – FS 75 Ba 4; 3 – FSA 15; 4 – FSA 30; 5 – FSA 30Mn1; 6 – A-98CaMg; 7 – AB 86

When the temperature increases from 90 to  $130^{\circ}\text{C}$ , the reaction rate increases significantly for the silicon-based alloys (FS 75 Ba 1 and FSA 30), however it slightly decreases for aluminium alloys A-98CaMg and AB 86. This reduction of the rate is associated with aluminium hydroxide formed on the surface of the particles. The hydrogen evolution rate for FSA 15 alloy is  $W_{\text{max}}=0.19\cdot 10^{-3}$   $\text{m}^3/\text{kg}\cdot\text{s}$  and the reaction completeness  $\alpha_{\tau}=0.53$  (the particles size lies in the range of  $(0.1-0.5)\cdot 10^{-3}$  m and the NaOH concentration of 13.3%).

The AB 86 aluminium alloy interacts with water instantly, but after a while, the resulting aluminium hydroxide begins to absorb water. Thus, the

aluminium alloys require a twofold increase in water consumption. In this regard, it is desirable to limit the concentration of aluminium in FSA alloys at the level of 25–30%.

An increase in the temperature to  $130^{\circ}\text{C}$  causes an increase in both the reaction completeness by 1.5–2.0 times and the reaction rate for the most alloys (Tables 1 and 2). The reaction products are silicon compounds of iron, barium and other impurities that can be destroyed only at elevated temperatures.

FS 75 Ba 1 alloy is much more active than FS 75 Ba 4 alloy. This is due to the fact that with increasing the aluminium content from 2 to 10% the volume of gas emission is reduced by 40–45% for the alloys containing barium [3,4].

Figure 3 shows time dependences of pressure

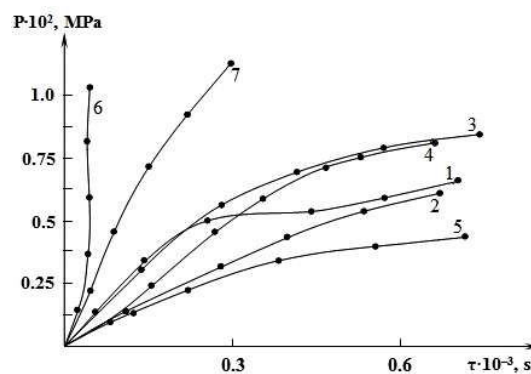


Fig. 3. Changes of pressure in the reactor with time during the interaction of alloys with 13.3% NaOH solution ( $m=1\cdot 10^{-3}$  kg): 1 – FS 75 Ba 1; 2 – FS75 Ba 4; 3 – FSA 15; 4 – FSA 30; 5 – FSA 30 Mn1; 6 – A-98CaMg; 7 – AB 86

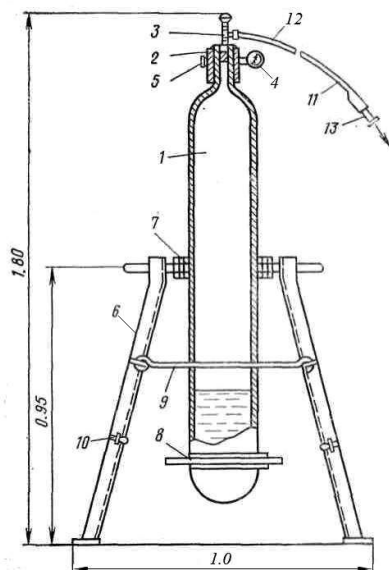


Fig. 4. AVG-45 balloon gas generator: 1 – reactor; 2 – head; 3 – valve; 4 – pressure gauge; 5 – safety valve; 6 – tripod; 7 – upper ring with a half-axis; 8 – lower ring with arms; 9 – large folding hook; 10 – small folding hook; 11 – rubberized-fabric hose; 12 – hose tip with cap nut; 13 – hose connecting branch

in the laboratory reactor during the interaction of alloys with aqueous solution of sodium hydroxide.

The reactions of the FS 75 Ba 1, FS 75 Ba 4, FSA 15, FSA 30 and FSA 30 Mn1 alloys were studied in the AVG-45 industrial gas generator (Fig. 4). Before the experiments, the alloys and granular caustic soda (sodium hydroxide) powder were put into the gas generator; then the required amount of water was added.

It was found that the temperature grows from 10°C to 40°C when 0.8 kg of granular caustic soda was dissolved in 6 L of water. A further temperature increase up to 70°C was due to the addition of a small amount of aluminium powder, since it promotes a subsequent reaction between silicon and caustic soda.

In case of FSA 30 Mn1 alloy, we used

$30 \cdot 10^{-3}$  kg of aluminium alloy based on A-98CaMg ( $d=(0.1-0.5) \cdot 10^{-3}$  m) to heat the reactor. This results in rapid water boiling during the first seconds of the reaction. Therefore, the amount of A-98CaMg alloy was reduced to  $20 \cdot 10^{-3}$  kg in further experiments. To provide the required reaction rate and reaction completeness, the following quantities of reagents are required: 1.25 kg of FSA (FS), 0.8 kg of NaOH, and 6 L of H<sub>2</sub>O [3].

The results of the study of FSA alloys and barium-containing alloys are shown in Table 3 and Fig. 5. The particle diameters were  $(0.3-1.2) \cdot 10^{-3}$  m,  $(0.1-0.52) \cdot 10^{-3}$  m, and  $(0.63-1.5) \cdot 10^{-3}$  m for the FS 75 Ba1/FS 75 Ba4, FSA 30/FSA 30 Mn1, and FSA 15 alloys, respectively.

The obtained results indicate that the highest reactor performance is observed when using the FS 75 Ba1 alloy. For the interaction of the FSA 30 Mn1 alloy with 13.3% solution of caustic soda in an autonomous gas generator AVG-45 of the balloon type, the reaction completeness is equal to 80%, which is practically twice as much as for the laboratory experimental data (43%) (Table 2). Maximum temperatures (240°C and 258°C) were detected in cases of FS 75 Ba1 and FSA 30 Mn1 alloys (Table 3).

The gas temperature in the upper part of the gas generator changes from 90°C to 105°C during the reaction and decreases up to 50°C at the external cooling.

It was established that it is impossible to unload the products of FSA 15 alloy interaction from the gas generator. This is partly due to a low temperature of the process. The unreacted iron- and silicon-containing compounds are burned in the internal surface of the gas generator. The reaction products of the barium-containing alloys FS 75 Ba1 and FS 75 Ba4 are freely removed from AVG-45 gas generator due to destruction of barium silicide (BaSi<sub>2</sub>) layer at increasing reaction temperature:

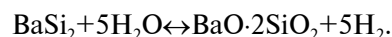


Table 3  
Test results of hydrogen generation in AVG-45 gas generator using FS 75 Ba1, FS 75 Ba4, FSA 15, FSA 30 and FSA 30 Mn1 alloys

Type of alloy	Concentration of NaOH, wt. %	Maximum temperature in the reaction zone, °C	Pressure in the reactors, MPa	Total reaction time, min	Released hydrogen volume, m <sup>3</sup>
FSA 30 Mn1	13.3	258	5.4	40	1.31
FSA 30	13.3	174	3.75	58	1.03
FSA 15	13.3	164	3.76	69	0.97
FS 75 Ba1	10.0	240	5.62	25	1.64
FS 75 Ba4	13.3	145	4.31	32	1.14

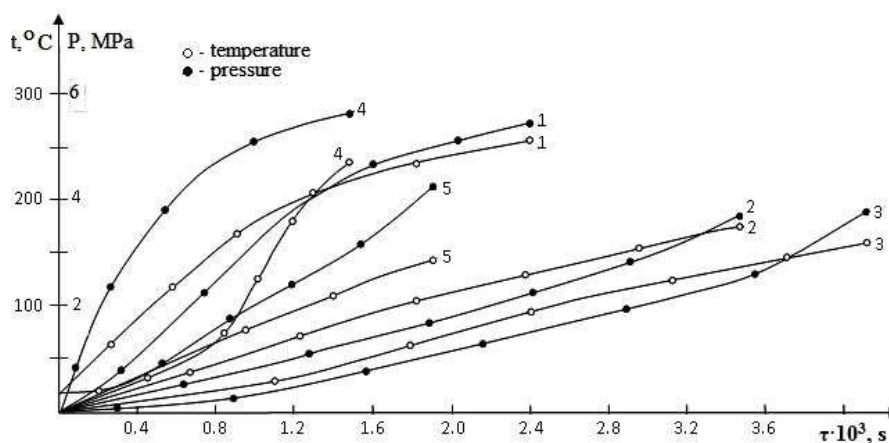


Fig. 5. Changes of pressure and temperature in the AVG-45 gas generator with time for the following alloys: 1 – FSA 30 Mn1; 2 – FSA 30; 3 – FSA 15; 4 – FS 75 Ba1; 5 – FS 75 Ba4

The possibility of chemical and phase transformations in the system is determined by the Gibbs-Helmholtz equation:

$$\Delta G = \Delta H - T\Delta S,$$

where  $\Delta H$  is enthalpy change;  $\Delta S$  is the entropy change; and  $T$  is the temperature.

Since the heterogeneous reactions in our case occurs at elevated pressure, the Gibbs energy values can be calculated taking into account the effect of pressure changes in the gas generator [7] as follows:

$$\Delta G = \Delta G^0 + RT \ln(P_2/P_1),$$

where  $\Delta G^0$  is the Gibbs energy in the standard state;  $R$  is the universal gas constant;  $T$  is the temperature; and  $P_2$ ,  $P_1$  are the final and initial pressure values in the apparatus, respectively.

The results of our calculations of the Gibbs energy values are given in Table 4.

The negative values of the Gibbs energy indicate the high probability of the gas evolution reactions in the course of the interaction of the considered ferrosilicon and ferrosilicon-aluminium alloys with aqueous NaOH solution.

It is well known that  $Al_2O_3$  film is formed on the surface of aluminium that prevents the interaction of a metal with alkali water solution. To provide a high rate of the dissolution of aluminium, it was advisable to apply a thin layer of metallic sodium to the surface of aluminium granules. However, this will significantly complicate the procedure of reagents preparation.

Therefore, to use non-deficient components as hydro-reacting substances (HRSs) and reduce the manufacturing cost, composite HRSs were developed that are based on aluminium powder with the additives of sodium hydride NaH (from 23 wt.% to 50 wt.%). The composite was synthesized by the pressing of these components and is further referred to as aluminium-hydride-sodium composite (AHSC).

The characteristics of the interaction of the HRSs with water were studied by means of a UD-40 installation (Fig. 6) at the pressure of to 4.0 MPa.

The installation UD-40 contains a reactor (1), which is fabricated in the form of a sealed steel tank with the volume of 300 L, which is partially filled with water during the experiments. The reactor cover was equipped with an ejecting device (2) with the hydro-reacting substances samples (3) fixed, and an electrical sealed connector (4) with connected

Table 4

**Thermodynamic data of the reactions between the alloys and water**

Type of alloy	Temperature of medium in the gas generator, °C	Gibbs energy for the standard state, $\Delta G^0$ , kJ/kg	Specific Gibbs energy, $\Delta G$ , kJ/kg
FS 75 Ba1	45	-5896.1	-5865.8
FS 75 Ba4	100	-7225.0	-7202.9
FSA 15	70	-9516.8	-9488.1
FSA 30	120	-8747.3	-8718.6
FSA 30 Mn1	123	-7535.5	-7495.5

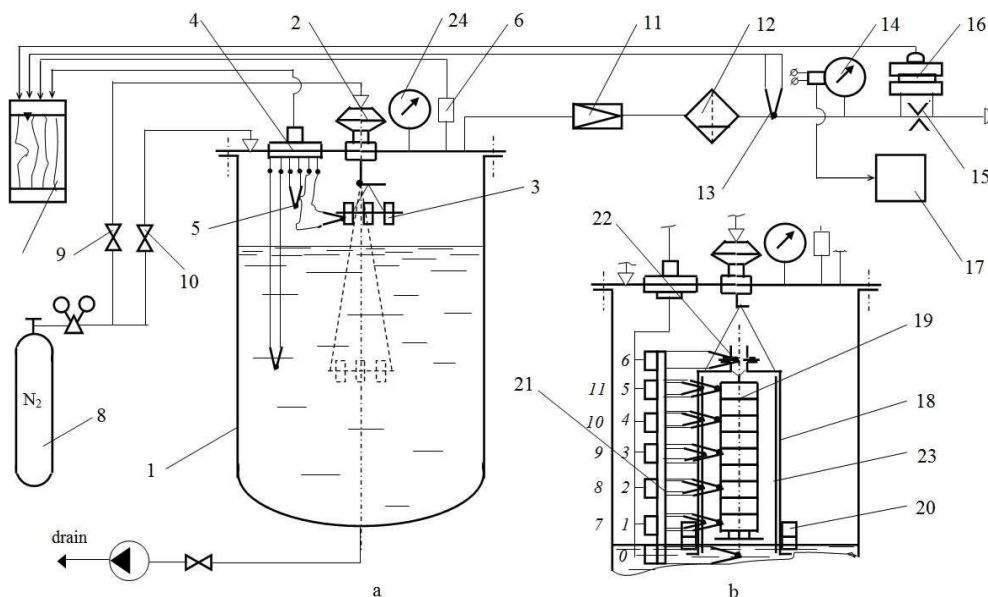


Fig. 6. Scheme of the UD-40 installation for study of the heat and mass transfer at pressures up to 4.0 MPa:  
 a – HRS and b – system for storage and supply of hydrogen. 1 – reactor; 2 – samples of HRS; 3 – ejecting device;  
 4 – electrical sealed plug; 5,13 – thermocouples; 6 – pressure sensor; 7,17 – recording devices; 8 – balloon;  
 9 – pressure reset control stopcock; 10 – N<sub>2</sub> gas purging stopcock; 11 – reducing valve; 12 – moisture removing filter;  
 14, 24 – manometers; 15 – diaphragm; 16 – differential pressure gauge; 18 – generator model; 19 – HRS column;  
 20 – ballast; 21 – thermocouple stand; 22 – throttling orifice; 23 – heat insulation

thermocouples (5) to measure water temperature in the reactor. The pressure in the reactor was controlled by the pressure gauge (21) of MP-5 type with a scale of 0–60 kg f/cm<sup>2</sup> and by the pressure sensor (6) of DD-10 type. The readings were registered by a recording device (7) which was equipped with a twelve channel loop oscilloscope H-117. The procedure for these experiments was similar to that described elsewhere [8–10].

The following AHSC samples were taken for the study: AHSC-23 containing 23 wt.% of NaH, AHSC-50 containing 50 wt.% of NaH and 5% of binder polyethylene and the samples of sodium aluminium hydride NaAlH<sub>4</sub> (AHS).

The test samples were cylindrical elements in the form of tablets with the outer diameter of 46 mm and the height of 7 mm to 20 mm with a central hole having the diameter of 10 or 11 mm. The tablets were manufactured by pressing. Their weight was ranged from 12 g to 35 g.

The volume of generated hydrogen, reduced to normal conditions, was determined from the pressure drop  $\Delta p$  onto the diaphragm (15) according to the following equation:

$$V_{sp} = 0.785\alpha\epsilon d^2 \sqrt{\frac{2\Delta p}{\rho_c}},$$

where  $d$  is the diameter of diaphragm aperture (m);

$\rho_c = \rho_n \frac{(p_1 + p_b - p_{s.v.}) T_n}{T_1 p_n}$  is the density of dry hydrogen

at the pressure  $(p_1 + p_b - p_{s.v.})$  and the temperature  $T_1$  before diaphragm (kg/m<sup>3</sup>);  $\rho_n$  is the density of dry hydrogen at normal pressure  $p_n = 0.1013$  MPa and normal temperature  $T_n = 293$  K, kg/m<sup>3</sup>;  $p_b$  and  $p_{s.v.}$  are the atmospheric barometric pressure (Pa) and saturated water vapor pressure (Pa) at temperature  $T_1$ , respectively.

The main parameters of hydrogen evolution via interaction between aluminium–sodium HRS samples and water are shown in Table 5 and Figs. 7 and 8.

During the performed experiments, the water temperature in the reaction vessel varied from 5°C to 70°C. Nevertheless, the reaction rate remained unchanged. This indicated the external-diffusion character of the reaction mechanism. The HRSs samples reacted as the whole items with a constant rate independently of the temperature until a certain period of time. It corresponds to  $V_{sp} = 0.35$ – $0.42$  m<sup>3</sup>/kg. Then, the samples fell apart and reacted further as the fine-dispersed particles.

This phenomenon indicates the transition of the reaction kinetics from the diffusion region to the kinetic one. The diffusion kinetics is typical of

Table 5

**Characteristics of hydrogen evolution via interaction between aluminium–sodium HRS samples and water reduced to normal conditions**

Characteristic	Hydro-reactive substance		
	AHSC-23	AHSC-50	AHS
Theoretical output of H <sub>2</sub> per unit mass of HRS $V_t, \text{m}^3/\text{kg}$	1.000	1.040	1.606
Experimental specific gas release $V_{sp}, \text{m}^3/\text{kg}$	$0.78 \pm 0.04$	$0.76 \pm 0.06$	$1.53 \pm 0.04$
Induction time $\tau_{ind}, \text{s}$	<0.5	<0.5	<0.5
Rate of hydrogen evolution (with respect to surface unit), $v_s \cdot 10^2, \text{m}^3/\text{m}^2 \cdot \text{s}$	$72.7 \pm 0.9$	$78.1 \pm 1.6$	$42.5 \pm 1.5$
Rate of hydrogen evolution (with respect to mass unit) $v_m \cdot 10^2, \text{m}^3/\text{kg} \cdot \text{s}$	$4.33 \pm 0.2$	$3.27 \pm 0.3$	$2.78 \pm 0.2$
Rate of HRS output, $v_l \cdot 10^3, \text{m/s}$	$0.752 \pm 0.005$	$0.673 \pm 0.008$	$0.24 \pm 0.01$
Density of HRS, $\rho \cdot 10^{-3}, \text{kg/m}^3$	$1.24 \pm 0.06$	$1.57 \pm 0.06$	$1.13 \pm 0.04$

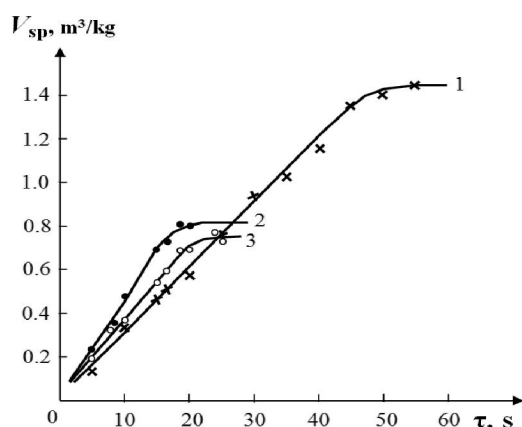


Fig. 7. Gas release generated by the aluminium–sodium HRS per unit of initial mass under normal conditions: 1 – AHS, 2 – AHSC-23, 3 – AHSC-50. Aluminium–sodium HRS samples were manufactured as tablets with the outer diameter of 46 mm and the thickness of 15 mm

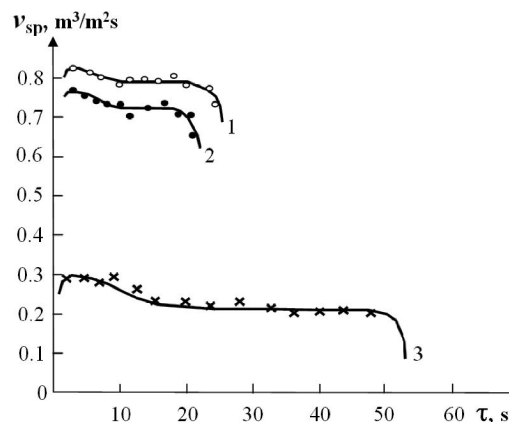


Fig. 8. Rate of hydrogen generation by the aluminium–sodium HRS per unit of initial mass under normal conditions: 1 – AHS, 2 – AHSC-23, 3 – AHSC-50. Aluminium–sodium HRS samples were manufactured as tablets with the outer diameter of 46 mm and the thickness of 15 mm

the samples being in a monolithic form. At the same time, the kinetic reaction region involves the reaction with the participation of scattered aluminium particles.

Study on the kinetics of reaction of aluminium hydride sodium at elevated pressure (up to 10 MPa) did not show any significant effect of pressure on the characteristics of the reaction with water. The limits of the experimental errors and variation did not exceed  $\pm 7\%$ .

It was found that the solid insoluble reaction products of the reaction between aluminium–sodium HRSs and water are colloidal-dispersed systems having different degrees of water content. According to the data of optical microscopy, the size of the particles was 1–250  $\mu\text{m}$ . The main bulk of these particles ( $\sim 70\%$ ) were characterized by the sizes of 50–100  $\mu\text{m}$ . The trial experiments conducted with such samples of the aluminium–sodium HRSs showed

a high rate of their reaction with water.

The self-cost of the HRSs production is relatively low and the components of the HRSs are available products. The developed technique for hydrogen generation was adopted as a base one for the development of hydrogen storage and supply systems, in particular for the autonomous lifting devices to lift the sunken objects off the ocean bottom.

The possibility for organizing a controlled process of hydrogen generation with the help of HRSs opens the ways to create new means of travel, the principle of action of which is based on the alternating change in positive and negative buoyancy. The positive buoyancy of objects immersed in an aquatic environment can be promoted by displacing fluid by gaseous hydrogen.

#### Conclusions

1. With increasing the temperature from 90 to 130°C, the reaction rate appreciably increases in case

of the silicon-based alloys (FS 75 Ba1, FSA 30) and slightly decreases for the aluminium alloys (A-98CaMg and AB 86). A decrease in the rate is associated with the formation of aluminium hydroxide on the particles surface.

2. The highest rate and the completeness of the reaction is observed for the alloys based on aluminium (A-98CaMg and AB 86). The content of aluminium in the FSA alloys should not exceed 25–30% to generate hydrogen in the balloon reactors.

3. It is impossible to unload the products of the interaction of FSA 15 alloy from the gas generator. This is partly due to a low temperature of the process. Unreacted iron-silicon compounds are burned on the internal surface of the gas generator. The products of the reaction of FS 75 Ba1 and FS 75 Ba4 barium-containing alloys are freely removed from AVG-45 gas generator due to the destruction of barium silicide ( $\text{BaSi}_2$ ) layer and the increase in the reaction temperature.

4. The use of alloy containing barium additives (FS 75 Ba1) allows facilitating the removal of the reaction products, reducing the emissions of the harmful substances into the environment and simplifying the design of gas generator.

5. The solid insoluble reaction products of the reaction between aluminium-sodium HRSs and water are colloidal-dispersed systems having different water content. These samples showed a high rate of the reaction with water and satisfactory indices of specific gas evolution.

6. The self-cost of the HRSs production is low and their components are easily available products. The developed technique of hydrogen generation can be used for the development of hydrogen storage and supply systems as well as autonomous lifting devices.

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Received 02.03.2020

## ГЕНЕРАЦІЯ ВОДНЮ З ВОДИ З ВИКОРИСТАННЯМ СПЛАВІВ НА ОСНОВІ КРЕМНІЮ І АЛЮМІНІЮ

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*Розглянуто процес одержання водню з води за допомогою сплавів на основі алюмінію та кремнію з добавками лужноземельних металів. Встановлено значення ступеня завершеності реакції взаємодії сплавів, що розглядаються, з розчинами  $\text{NaOH}$  зі змінною концентрацією (від 10% до 13,3%) в інтервалі початкових температур від 90°C до 130°C. Встановлено, що необхідний вміст алюмінію в феросилікоалюмінієвих сплавах повинен бути 25–30% для того, щоб інтенсифікувати процес виділення водню в лабораторному реакторі об'ємом  $1,13 \cdot 10^{-3}$  м<sup>3</sup>. Зі сплавами феросиліцію та феросилікоалюмінію проведено дослідження в автономному газогенераторі АВГ-45 балонного типу. Розраховано значення енергії Гіббса з урахуванням впливу зміни тиску в газогенераторі. Надано рекомендації з застосування силіколевого способу генерації водню в водневих газогенераторах із використанням алюмокремнієвих сплавів. Здійснено дослідження алюмогідриднатрієвих сумішей композитів з вмістом  $\text{NaH}$  23 мас.% і 50 мас.% та зразків алюмогідрида натрію  $\text{NaAlH}_4$  з водою для застосування в водневих генераторах. Методика одержання водню з використанням гідрореагуючих речовин запропонована як базова для застосування в системах генерації водню та в розроблюваній системі зберігання і подачі водню в експериментальних зразках автономних підйомних апаратів.*

**Ключові слова:** феросиліцій, феросилікоалюміній, водень, вода, алюмогідрид.



**HYDROGEN GENERATION FROM WATER BY USING ALLOYS BASED ON SILICON AND ALUMINIUM**

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We considered the process of hydrogen generation from water by using the alloys based on aluminium and silicon with the alloying additions of alkaline earth metals. The degree of completeness of the interaction between the above alloys and NaOH solution (10–13.3%) was determined for the range of initial temperatures of 90°C to 130°C. The required aluminium content in the ferro-silicon-aluminium alloys should be about 25–30% to intensify the hydrogen generation process in a laboratory reactor with a volume of  $1.13 \cdot 10^{-3} \text{ m}^3$ . The reactions of ferro-silicon and ferro-silicon-aluminium alloys with water were investigated in an AVG-45 autonomous balloon-type gas generator. The Gibbs energy value was calculated taking into account the influence of pressure changes in the gas generator. Recommendations have been developed to apply a silicone method of hydrogen generation in the hydrogen gas generators using aluminium-silicon alloys. The interaction of aluminium-sodium hydride composites with the NaH content of 23 wt.% and 50 wt.% as well as the samples of sodium aluminium hydride (NaAlH<sub>4</sub>) with water was studied to use them in the hydrogen gas generators. The procedure of hydrogen generation by means of hydro-reactive substances was adopted as a basic one to use in the hydrogen generation systems and in the developed system of hydrogen storage and hydrogen supply in experimental samples of the autonomous lifting installations.

**Keywords:** ferrosilicon; ferrosilicon-aluminium; hydrogen; water; aluminium hydride.

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