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CHARACTERISTIC FEATURES OF CALCULATIONS OF HYDROGEN GENERATORS

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Among the methods of hydrogen generation that are economically sound for autonomous customers is the silikol method. The technique of calculation of the cylinder gas generator circuit is given. The restrictions imposed on the flow velocity in a three-phase reacting system are considered. It is established that the reaction rate in the circuit as a dissipative structure is in direct correlation with the change in the Gibbs energy.

Keywords: *hydrogen, technique of gas generator calculation, Gibbs energy.*

Introduction. At present there is substantial interest in hydrogen power engineering. This has prompted the search for new methods of obtaining hydrogen and improving the available ones.

Among the techniques of hydrogen generation economically sound for autonomous customers is the silikol method. Here, one makes use of the ability of certain alloys to displace hydrogen from water by applying, in particular, the industrially produced alloy FS75 (wt. %: Si, 75; Fe, 25).

Experiment and Calculation Technique. Tests of cylinder-type gas generators made it possible to improve the process and recommend for application the FSA alloy (wt. %: Si, 60–62; Al, 15–30; Fe, the rest) [1–3]. The alloy is obtained from the inorganic portion of low-caloric coals and coal waste, which in turn makes it possible to produce hydrogen more cheaply and introduce unbalanced coal into the turnover [4, 5].

The basic physicochemical and hydrodynamic laws governing the process of hydrogen production have been established [6, 7]. As a result of the reaction of alumosilicic alloys with water, an appreciable amount of heat is evolved, which leads to the formation of water vapor. At a low pressure the flow in the ascending channel is determined by vapor, whereas on increase in pressure, by hydrogen. In the former case the ascending channel in the reactor can be considered as an evaporator.

Common to the methods of calculations of evaporators and reactors are:

a) methods of determining the theoretical velocity of adiabatic gas and vapor flows in the channels of natural-circulation apparatuses;

b) estimation of the resistance of channels to the motion of two-phase flows;

c) techniques of using the symmetry and asymmetry trends in construction of apparatuses and their assemblies.

One observes differences in the selection of the constituents of kinetic equations and in the calculation of the velocity of gas-liquid flow motion near the heat- and mass transfer surface moving in gas generators and fixed in evaporators [8, 9].

The characteristic features of heat and mass transfer in gas generators are:

a) a substantial influence of the Reynolds number of a gas-liquid flow and alloy density on the rate of hydrogen evolution from water;

b) restriction on the velocity of gas-liquid flow motion imposed by the speed of sound;

c) a substantial resistance to heat transfer offered by the originating oxidic layer.

In designing apparatuses, one composes regulations containing the physicochemical constants and properties of substances, stoichiometric and kinetic relations, material and thermal balances. A certain type of a gas generator is also selected. Thus, it is considered that the following quantities are given: the mass G and volume V of a reacting substance fed to the reactor per cycle; the mass G_{H_2} and volume V_{H_2} of hydrogen obtained per cycle; the mass G''_{H_2} and bulk V''_{H_2} efficiencies of a generator based on hydrogen; volume of water V_w expended per cycle; volume of solid

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product of reaction V_{pr}; phenomenological coefficient L of the rate of hydrogen evolution (according to the data of kinetic investigations); the total f and specific f_{sp} surface areas of the alloy powder; R_{par}, radius of one alloy particle; ν''_{H_2}, quantity of hydrogen evolved per unit mass of an alloy; q, quantity of heat formed per unit mass of hydrogen; F_{ap}, cross-sectional area of the apparatus, and h, the height of the liquid level.

In the first approximation the induction and final periods of reaction are not taken into account. In such a case the average rate of hydrogen evolution W is close in value to the maximum one calculated by the Volmer–Gibbs equation [6, 8]:

$$W = LA \,, \tag{1}$$

$$A = \sum_{i,j} \nu_i \mu_i \quad (i = 1, ..., I\,;\ j = 1, ..., J)\,, \quad \mu_i = \left(\frac{dG}{dm_i}\right)_{P,T,m_i \neq m_j} .$$

The chemical potential of the ith component in a multicomponent mixture represents a change in the Gibbs free energy of a mixture on introduction into it of a unit mass of the ith component at constant temperature, pressure, and concentration (mass) of other components. The chemical technology usually employs the dimensionality J/mole for μ_i. However, in the practice of the manufacture of gas generators it is more convenient to use the dimensionality kJ/kg, i.e., the value of chemical energy related to 1 kg of the active portion of an alloy.

Using the height of the pulp level h, the superheating of liquid in the lower part of the apparatus is determined. The speed of the vapor-liquid mixture efflux in adiabatic boiling up of liquid v is calculated from the change in enthalpy. The actual discharge velocity of the flow v^* can be found from the relation [10]

$$v^* = \varphi v \ (0.75 < \varphi < 0.87)\,. \tag{2}$$

Relation (2) is applied proceeding from the assumption that the relative effective efficiency of the ascending channel is

$$\eta_{\mathrm{r.ef}} = \varphi^2\,. \tag{3}$$

The average flow velocity in the ascending channel (according to experimental data) is

$$v_{\mathrm{av}} = \frac{2}{3} v^*\,. \tag{4}$$

Using the known value of W, the corresponding quantity of heat Q evolved in the course of reaction is determined. The mass of the vapor formed is given by the equation

$$G'' = Q^*/r\,, \quad Q^* = Q - Q_{\mathrm{h.e}}\,.$$

With the use of the mass of the vapor, its volume is determined:

$$V'' = G''/\rho'',$$

which makes it possible to evaluate the cross-sectional area of the ascending flow:

$$f_{\mathrm{as.fl}} = V''/v_{\mathrm{av}}\,.$$

Next, the Reynolds number of the ascending flow liquid is determined by the method developed for evaporators, with the diameter of the ascending channel being the determining dimension in the criterion. From the Re number and experimental data the real value of the coefficient L^* is determined [6, 11, 12].

Previous investigations have shown that an increase in the dimensions of apparatuses and density of alloy particles leads to an increase in the flow circulation nonuniformity and to a decrease in the intensity of gas evolution, which is reflected in the values of the coefficient L^* [6].

Next the real rates of hydrogen evolution W^* and bulk efficiency of the reactor $V^*_{\mathrm{H}_2}$ are calculated in succession:

$$W^* = L^* \mu f_{\mathrm{sp}} \,, \quad V^*_{\mathrm{H}_2} = W^* f^* \,.$$

At the beginning of the process ($\alpha = 0.3$) the reaction surface of the powder is equal to

$$f^* = 0.3 f_{\mathrm{sp}} \,.$$

The coincidence between the given value of the bulk efficiency $V^*_{\mathrm{H}_2}$ and the predicted one means that the reaction volume was selected correctly. Additionally the liquid level in the apparatus at the end of the reaction h^* and the circulation ratio z are calculated:

$$h^* = V_{\mathrm{p}} / F_{\mathrm{ap}} \,.$$

It should be taken into account that the liquid level in the apparatus depends on volumes of the solid products of reaction and water poured into the apparatus minus the amount of water evaporated and expended on the reaction itself.

Since there is an excess of water in the gas generator relative to the stoichiometric amount, hydrogen is saturated with water vapor. The moisture content of the vapor-gas mixture is determined from the well-known relation [13]. For normal operation of the gas generator the following condition should hold:

$$h^* \cong h \,.$$

The circulation ratio corresponds to the expression allowing for the lifetime of an alloy particle τ_{par} and the time taken by the particle to pass through the circulation circuit $\tau_{\mathrm{c.c}}$:

$$z = \tau_{\mathrm{par}} / \tau_{\mathrm{c.c}} \,, \quad \tau_{\mathrm{par}} = V''_{\mathrm{par}} / (W f^*_{\mathrm{par}}) \,, \quad f^*_{\mathrm{par}} = 0.5 f_{\mathrm{par}} \,, \quad V''_{\mathrm{par}} = v''_{\mathrm{H}_2} m_{\mathrm{par}} \,, \quad m_{\mathrm{par}} = \rho V_{\mathrm{par}} \,.$$

To calculate individual periods of the process it is advisable to use the Erofeev equation that allows for the probability of the interaction of the given system molecules [14]:

$$\alpha = 1 - \exp\left(- k \tau^n\right) .$$

In this case, the arithmetic mean reaction surface is replaced by the integral mean one.

An increase in pressure with simultaneous cooling of the gas generator precludes the boiling-up of water. In this case the hydrodynamic situation in the apparatus is determined by the hydrogen flow. The limiting velocity of liquid circulation practically cannot exceed the value of the local speed of sound [15]:

$$v_{\max} = \frac{1 + U_{\mathrm{as.fl}}}{\sqrt{(U_{\mathrm{as.fl}} \rho_{\mathrm{H_2O}}) / P_{\mathrm{g}}}} \,. \qquad (5)$$

Equation (5) is suitable for calculating not only vapor-liquid flows, but also gas-liquid ones. The real velocity of flow discharge is determined with allowance for the nozzle efficiency determined from the slip coefficient of phases [10]. Relation (5) was developed for jet apparatuses. In our case, an ascending channel in an apparatus with natural circulation is considered. Since the velocity of circulation is related to the gravitational field intensity, it is necessary to use dependences for air gaslifts.

As is known, with increase in the gas flow rate in the channel of a gaslift the amount of the liquid carried out first increases to a known limit and then gradually decreases. With decrease in the diameter of the ascending tube the efficiency of the air gaslift increases. The magnitude of the efficiency is defined by the ratio of the useful work to the work done by a working agent [16, 17]. There is a simplified dependence to calculate the moisture content in an ascending flow [18, 19]:

$$(1-\psi)=\frac{0.01\mu_{H_2O}^{0.3}+0.14}{d_{\text{as.fl}}^{0.34}v_{\text{g.red}}^{0.48}}.$$

Subsequently this equation is to be nondimensionalized.

The amount of the lifted liquid is determined with allowance for the resistance of the ascending channel and for the friction caused by the slip of phases. The equation makes it possible to find the amount of the liquid raised by a gaslift, which in turn allows one to estimate the regimes of flow past the alloy particles. Here it is necessary to take into account the value of the drag coefficient of a sphere (alloy particles) depending on the Re number [20].

To describe heat exchange between a fixed spherical particle and the liquid around it the Katsnel'son–Timofeeva [21], Kunii–Levenspiel [22], and Gel'perin–Kvasha [23] relations are used. The processing of experimental data by the relations suggested by the above-named researchers showed that the Kunii equation yields the smallest deviations, while the Katsnel'son–Timofeeva relation yields the greatest ones. In the enumerated equations the exponent at the Re number changes within 0.5–0.58. When $Re < 200$, an increase in the flow velocity causes a decrease in the width of the decelerated region behind the sphere. This leads to an increase in the heat transfer intensity despite the fall in the drag coefficient [24]. With further increase in the Reynolds number the flow around the sphere acquires a pulsating character, which leads to an increase in the drag coefficient. In this case the degree of influence of the Reynolds number on the heat transfer coefficient increases from 0.5 to 0.58.

In the case of a flow around a reacting particle the exponent at the Reynolds number attains 1.3–1.79 [25]. With increase in the flow velocity around the sphere the rate of vapor and gas formation increases, which is accompanied by the boundary layer turbulization. Close conditions of heat and mass transfer are observed on water evaporation into its own superheated vapor [26]. After the calculation of the Re number, the heat transfer coefficient is determined.

To estimate the specific heat loading q, the temperature head between the alloy particles and solution is determined. Using the pressure in the gas generator, the critical pressure of gas efflux is determined [27]. Next, in the absence of the solution boiling up, the limiting velocity of gas efflux is determined from Eq. (5) and then the average velocity of flow from Eq. (4) [28]. The temperature of the solution is determined from the heat balance that allows for the heating of the interacting products and of the apparatus walls [3]. To the found value of q there corresponds a certain value of the rate of the process W. The value of W is used to refine the value of the Gibbs specific energy ΔGi, which in turn allows one to correct the value of the coefficient L. In view of the fact that the value of the Gibbs energy depends on pressure, in the third approximation it is necessary first to determine its value from the formula [29]

$$\Delta Gi=\Delta Gi^{\circ}+RT\ln\left(P_f/P^{\circ}\right),$$

and then to refine the value of the coefficient L.

The geometric dimensions of the circuit, the dispersity of the alloy powder, and the temperature and pressure of the reaction are varied until coincidence between the quantity of heat determined from the equation of convective heat transfer and the kinetic dependence of chemical reaction. This excludes the possible limitation of the reaction rate by heat removal. Some details of the work were discussed in [1, 6, 9, 11, 12].

Conclusions. The previous investigations showed that with increase in the diameter of the apparatus the heat and mass transfer rate drops, which is expressed as an increase in the absolute value of the negative exponent at the Re number. The provision of a pulsating regime considerably intensifies the process. On finding the optimal geometric dimensions of the apparatus, the intensity of the process is enhanced by selecting the composition of alloys and changing their structure. The developed model of the process includes gas dynamic laws in combination with the kinetic ones expressed in terms of chemical potentials. Moreover, the intensity of heat exchange between the phases is estimated. The allowance for the thermodynamic and kinetic factors raises the reliability of the technique of calculation of hydrogen generators.

NOTATION

A, chemical reaction affinity; *d*, diameter, m; *F*, cross-sectional area, m^2; *f*, surface area of alloy powder, m^2/kg; *G*, mass of reacting substance, kg; G''_{H_2}, mass flow rate, kg/sec; Gi, Gibbs energy, J; *h*, height, m; *k*, constant of the rate of growth of vapor (gas) phase depending on temperature; *L*, proportionality factor, $m^3/(m^2\cdot sec\cdot J)$; *m*, mass of mixture component, kg; *n*, constant characterizing geometric elements of the heat transfer surface on which vapor (gas) bubbles nucleate; *P*, pressure, Pa; *Q*, heat, J; *q*, heat flux density, W/m^2; *R*, universal gas constant, 8.314 J/(mole·K); Re, Reynolds number; R_{par}, alloy particle radius, m; *r*, vapor generation heat, J/kg; *T*, temperature, K; *U*, ratio of the volumes of gas and liquid; *V*, volume, m^3; V''_{H_2}, bulk flow rate, m^3/sec; *v*, velocity, m/sec; *W*, rate of hydrogen evolution, m^3/(kg·sec) or $m^3/(m^2\cdot sec)$; *z*, circulation ratio; α, extent of substance conversion; Δ, change of the final value; $\sum$, summation over all the phases and substances participating in reaction; η, efficiency; φ, slip coefficient of phases; μ, dynamic coefficient of viscosity, Pa·sec; μ_i, chemical potential, J/kg; ν, stoichiometric number of moles; ρ, density, kg/m^3; τ, time, sec; ψ, gas content, kg of dry gas/kg of water-gas mixture. Subscripts and superscripts: ap, apparatus; as.fl, ascending flow; av, average; c.c, circulation circuit; g, gas; f, final; h.l, heat losses to heat up the reactor and mixture of reagents; *i*, *j*, phase and components of the given phase participating in the reaction; p, pulp; par, particle; pr, reaction products; r.ef, relatively effective; red, reduced; sp, specific value; w, water; ′, liquid; ″, vapor; *, real experimental value; °, values of quantities under normal conditions (P = 0.1 MPa, T = 298 K).

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