Axisymmetric hydrate monolith destruction problem

M V Stolpovsky, A S Chiglintseva and M R Davletshina

Ufa State Petroleum Technological University, 1, Kosmonavtov str., Ufa,450062, Russia

1 E-mail: davletshina@yandex.ru

Abstract. A mathematical model is proposed for the destruction of a methane hydrate monolith containing gas inclusions. In this formulation of the problem, it is assumed that there is a cylindrical cavity inside the hydrate monolith, initially filled only with methane. Since the conditions on the surface of the particle correspond to the conditions for the free existence of gas and water, the gas hydrate begins to decompose. On the basis of the obtained system, consisting of the equations of conservation of mass and heat, the temperature distributions in the "cavity - gas hydrate" system were obtained, and the influence of the initial temperature of the system and the temperature in the cavity on the dynamics of hydrate decomposition was analyzed.

1. Introduction

At the bottom of lakes, seas and oceans, huge reserves of hydrocarbons are concentrated. The most important component of hydrocarbon raw materials, natural gas methane, is contained in bottom sediments in a dissolved form. But under certain conditions, dissolved methane can, interacting with water, form solid formations - methane hydrates [1]. This requires a high concentration of dissolved methane, high pressure and low temperature. The last two conditions are usually met in water areas at depths of more than 300-500 m. Where the concentration of methane is high enough, gas hydrates are formed.

At present, a huge number of sources of gas (methane) release from the surface of the seabed are known [1, 2]. Similar manifestations of gas release in the form of bubbles were also observed at Lake Baikal [3, 4]. It should be noted that the emergence of such methane bubbles was accompanied by the appearance of a gas hydrate shell, which is due to the low temperatures of the surrounding water and high hydrostatic pressure. From visual observation of pieces of a natural gas hydrate monolith (delivered from the bottom of Lake Baikal, for example) when rising in water, one can see their decomposition (cracking) into smaller pieces [3, 4]. It seems that such a picture of the destruction of hydrates is similar to the process of volumetric boiling of superheated water. As is known, according to the basic concepts, boiling of a metastable liquid occurs due to the presence in it of various particles (gas microbubbles, for example), which serve as nuclei of vaporization. Similarly, it can be assumed that natural monoliths of methane gas hydrate also contain many gas inclusions in the form of small spherical or cylindrical bubbles, as well as in the form of closed cracks.

A theoretical study of the formation and decomposition of gas hydrate particles during their ascent in water is considered, in particular, in works [5, 6]. Mathematical models of the injection of carbon dioxide into gas hydrate formations for the purpose of methane production are presented, in particular, in [7–9]. Some features of the formation and decomposition of gas hydrates in porous media of semi-infinite extent are considered in [10 – 12] This paper presents a model of the destruction of a gas hydrate
particle in water when the inclusion has a cylindrical shape. On the basis of the obtained system, consisting of the equations of conservation of mass and heat, the temperature distributions in the “cavity - gas hydrate” system were obtained, and the influence of the initial temperature of the system and the temperature in the cavity on the dynamics of hydrate decomposition was analyzed.

2. Problem statement and basic equations

Consider an immobile hydrate particle in water and having a spherical cavity inside. Let's connect the origin of coordinates with the center of the particle. The initial radii of the cavity and the hydration particle are assumed to be equal to \( a_0 \) and \( a_h \), respectively. We also assume that the initial temperature \( T_0 \) of the “cavity - hydrate” system and the pressure corresponding to this value are in the region, satisfy the conditions for the free existence of a mixture of methane and its gas hydrate. With a decrease in the external pressure, caused, for example, by the rise of a particle, the thermodynamic parameters correspond to the conditions for the stable existence of gas (methane) and water, i.e. the particle is located above the upper boundary of the zone of stable existence of the hydrate. In this case, the decomposition of the gas hydrate particle occurs. In this case, the decomposition products of the hydrate (methane and water) are in a cylindrical cavity, and the hydration shell is in contact with the surrounding water, the temperature of which is \( T_0 \).

The heat conduction equation in the hydrate region (\( a < r < a_h \)) in the axisymmetric case has the form:

\[
\rho_h c_h \frac{\partial T}{\partial t} = \lambda_h \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right).
\]  

(1)

Here \( r \) – is the radial coordinate; \( t \) – time; \( T \) – temperature; \( \rho_i, c_i, \lambda_i \) – are the density, specific heat and thermal conductivity of the \( i \)-th phase, respectively; \( a \) – is the current radius of the cavities. Here and below, the subscripts \( i = h, g, l \) refer to the parameters of hydrate, gas, and water, respectively.

We will assume that the temperature in the cylindrical cavity follows the equilibrium temperature \( T_s \) dissociation of the gas hydrate, which depends on the current pressure. In accordance with this, you can write:

\[
t > 0, 0 \leq r \leq a : T = T_s(p).
\]  

(2)

The temperature on the surface of the hydrated particle is equal to the initial temperature \( T_0 \):

\[
t > 0, r = a_h : T = T_0.
\]  

(3)

Should be noted that, at small pressure drops, the equilibrium temperature is rather well approximated by a dependence of the form:

\[
T_s(p) = T_{h0} + T_s \ln \left( \frac{p}{p_{h0}} \right),
\]

where \( T_s \) – an empirical parameter that depends on the type of gas hydrate and on the considered ranges of temperatures and pressures; \( T_{h0} \) – equilibrium temperature corresponding to pressure \( p_{h0} \) [10 – 14]. In this work, only the thermal problem is considered, i.e. the case when the gas-hydrate particle is immobile in the liquid. This means that the pressure \( p \) is constant, i.e. the cavity temperature, as follows from (2), does not change.

The condition for heat balance on the moving surface of the phase transition (\( r = a \)) taking into account (2), has the form:

\[
\rho_l c_l \dot{a} = \lambda_l \left( \frac{\partial T}{\partial r} \right)_{r=a}.
\]  

(4)
Here $l_h$ – is the specific heat of decomposition of the hydrate; $a = \frac{da}{dt}$ – the speed of the front of the phase transition.

The equation of conservation of mass $m$ of the decomposition products of hydrate (gas and water) per unit length has the form:

$$\frac{dm}{dt} = 2\pi \rho_i a \dot{a}.$$  \hspace{1cm} (5)

On the other hand, the mass of gas and water in the cavity can be determined through the average density $\rho$ of the gas-liquid mixture:

$$m = \pi a^2 \rho.$$  \hspace{1cm} (6)

The average density of the gas-liquid mixture, which can be written as:

$$\rho = \rho_g \alpha + \rho_l (1-\alpha),$$

where $\rho_i$ ($i = g, l$) – the true density of the gas and water; $\alpha$ – is the volumetric gas concentration. Hereinafter, the subscript $i = g, l$ corresponds to gas and water.

If in the initial state ($t \leq 0$) there is only one gas inside the cavity, $\alpha$ will be a variable. Therefore, to obtain a closed system of equations, we add equations for changing the mass of water in the cavity, which for a cylindrical crack has the form:

$$\frac{dm_i}{dt} = 2\pi \rho_i (1-G) a \dot{a}.$$  \hspace{1cm} (7)

Here $G$ is the mass content of gas in the composition of the hydrate. On the other hand, for the mass of water contained in the cavity, you can write:

$$m_i = \pi a^2 \rho_l (1-\alpha).$$  \hspace{1cm} (8)

The gas will be considered calorically perfect with the equation of state:

$$p = \rho_g R_g T,$$

where $R_g$ – is the reduced gas constant. Hydrate and water are incompressible.

As initial conditions, ($t \leq 0$) we assume:

$$a = a_0, \quad p = p_0, \quad \alpha = 1, \quad T = T_0 \quad (0 \leq r \leq a_h).$$  \hspace{1cm} (9)

The solution of the presented system of equations was carried out by the finite-difference method using the algorithm for catching the front into a node of the spatial grid, considered in [8, 15].

3. Discussion

Figure 1. for the moment of time $t = 4$ and 7 min. the distribution of the “cavity – hydrate” system for the initial particle temperature $T_0 = 274$ K. For the remaining parameters characterizing the system, the following values are taken $c_h = 2100$ J/(kg·K), $\lambda_h = 2.45$ W/(m·K), $l_h = 5\cdot10^5$ J/kg, $\rho_h = 900$ kg/m$^3$, $\rho_l = 1000$ kg/m$^3$, $R_g = 520$ J/(kg·K), $G = 0.12$. The cavity temperature was assumed to be $T_c = 279$ K, which corresponds to the equilibrium decomposition temperature of the hydrate at a pressure of $p = 5$ MPa. The initial radii of the particle and the cavity were assumed to be equal to $a_h = 10$ mm and $a_0 = 1$ mm, respectively.

As follows from the figure, in the gas hydrate region, the temperature decreases from the maximum value at the edge of the cavity to the minimum value corresponding to the surface of the gas hydrate...
particle. Moreover, as follows from the statement of the problem, the temperature in the region containing gas and water is constant.

Figure 1. Temperature distribution of the "cavity - hydrate" system at times $t = 4$ min (1) and 7 min (2).

Figure 2 shows the time dependences of the masses of the mixture, water and gas (3) per unit length. The temperature in the mixture was assumed to be $T_s = 276.3$ K, which corresponds to a pressure of 3.8 MPa. As follows from the figure, with an increase in the initial temperature, the intensity of cavity formation decreases. This is due to the fact that the intensity of hydrate decomposition, limited by the supply of heat to the “cavity – gas hydrate” boundary, decreases with increasing temperature $T_0$. Therefore, due to the intensive decomposition of the hydrate, at lower values of $T_0$ the volume concentration of the gas in the cavity decreases faster than.

Figure 2. The dependence of the masses of the mixture (1), water (2) and gas (3) falling per unit length of time.

Figure 3 shows the dependence of the volume concentration of the gas cavity and the radius of time for different values of cavity temperature at $T_0 = 274$ K. The cavity temperature was assumed to be $T_s = 276.3$ K (corresponding to a pressure of 3.8 MPa). As follows from the figure, with a decrease in the cavity temperature (which corresponds to a decrease in pressure), the intensity of hydrate decomposition also decreases. This is due to the fact that with decreasing cavity temperature, the heat
flux directed to the decomposition of the hydrate also decreases. As a consequence, at higher values of $T_s$ the volume concentration of the gas in the cavity decreases faster.

![Figure 3](image)

**Figure 3.** Dependence of the cavity radius ($a$) and the volumetric gas concentration ($b$) on time at $T_s = 276.3$ K.

4. Conclusion
A mathematical model of the destruction of a gas hydrate particle in water, when the inclusion has a spherical shape, is presented. On the basis of the obtained system, consisting of the equations of conservation of mass and heat, the temperature distributions in the “cavity - gas hydrate” system were obtained, and the influence of the initial temperature of the system and the temperature in the cavity on the dynamics of hydrate decomposition was analyzed. It was found that with an increase in the initial temperature, the intensity of cavity formation decreases. It is shown that at higher temperatures in the cavity, the volumetric gas concentration in it decreases faster.

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