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MATHEMATICAL MODEL DECOMPOSITION OF GAS HYDRATES

Abstract: *The article presents the results of the study of the influence of pressure and temperature of the gas-water environment on the process of hydrocarbon gas hydration formation, occurring on its phase interface surface. A mathematical model is proposed to determine the optimum ratios of pressure, gas temperatures, water, and gas bubble sizes in the bubbling, gas ejection, or mixing processes. It was determined that there is a gas temperature range where the hydrate formation speed is maximum. The research findings can be used to optimize various technological processes associated with production of gas hydrates in the industry.*

Keywords: *gas hydrates, phase transformations, gas pressure, gas temperature.*

Statement of the problem

Marine gas hydrates considered most probable alternative fuel in many countries. Above their exploration and development work in France, Germany, USA; but especially active Canada and Japan. The Japanese plan to start commercial production of methane from the "Ice fuel" around their islands in the basin Nyanhay in 2016. Russia intends from 2020 to extract gas hydrates in industrial quantities. However, effective technology acquisition, storage and transport of methane gas hydrates as still in the development stage.

Overview of the latest sources of research and publications

Tasks unsteady heat conduction with moving boundary conditions called Stefan problems. Melting ice solidification metal solidification concrete – it's only a few examples of such problems. Solution of Stefan problem possible to the different ways. Typically for solving such problems using digital methods because of their analytical solution is possible only in the simplest cases. Analytical solutions of two-dimensional nonlinear heat conduction problems are known only for certain, relatively simple cases [1, 2]. The most universal way to solve them is to use digital techniques [3, 4], which can be easily implemented using computer technology. However, digital methods impose their limitations [5, 2]. For example, a tridiagonal matrix algorithm using implicit schemes have to solve a system of linear algebraic equations. Number of equations equal to the number of nodes and computational mesh can be quite large. In applying the implicit scheme in time step tridiagonal matrix algorithm relatively small, which increases the cost of machine time for calculation [6, 4]. Using the method of dynamic mesh adaptation requires a complex algorithm to implement. Applying the average value of coefficient of thermal conductivity on the boundary of materials with different properties and thermal properties when materials change also leads to a gradual accumulation of errors in calculations.

Selection of the unsolved parts of general problem

This work was to improve methods of storage and transportation of gas hydrates in equilibrium conditions. At atmospheric pressure and positive ambient temperature they gradually decompose gas

and water. Simulation of the decomposition of gas hydrates will determine the optimal conditions of transportation and storage, to minimize the loss of gas.

The purpose of work

The aim is to create a mathematical model of thermal processes occurring in the decomposition of gas hydrate.

The main material

Two-dimensional mathematical model of transient thermal conditions based on a linear equation Fourier thermal conductivity of specific is volume sources (or loss) of heat

$$c_{(x,y)}\rho_{(x,y)} \cdot \frac{dt_{(x,y)}}{d\tau} = \frac{\partial}{\partial x}\left(\lambda_{(x,y)}\frac{\partial t}{\partial x}\right) + \frac{\partial}{\partial y}\left(\lambda_{(x,y)}\frac{\partial t}{\partial y}\right) + q_{v(x,y)} \quad (1)$$

where:

c – heat capacity, J/(kg·°C);

ρ – density, kg/m^3;

t – temperature, °C;

λ – thermal conductivity, W/(m·°C);

q_v – volumetric heat source, W/m^3.

All these values are functions of spatial coordinates X, Y and temperature t.

To calculate the phase transition is necessary to set a number of conditions. The condition for the start of phase transition element is to achieve the phase transition temperature:

$$t_{(x,y)} \geq T_P \quad (2)$$

Temperature phase transition (T_P) consider constant:

$$T_P = \text{const} \quad (3)$$

For obtain unambiguous solution of this problem it is necessary to complement the geometric, physical, temporal and boundary conditions. Geometrical conditions determine the shape and size of the body, in which the study process. Setting the field of solid phase takes place by recording the corresponding index in the data array that matches a platform with known coordinates – are set point wise.

Physical conditions are set thermophysical parameters of body (λ, c_v, ρ) and distribution of internal heat sources $q_{v(x,y)}$. They are set apart for solid and gaseous phases, also point wise and can be corrected functional in the case depends of these values on other parameters (temperature, time, coordinates, etc.).

Time (initial) conditions include temperature distribution in the body at the initial time. We specify point wise (or regions) to separate solids and air, it washes:

$$t_{(x,y)} = t_{(x0,y0)} \quad (4)$$

Boundary conditions determine the features the process of passing the heat transfer on the surface of the body. The boundary conditions of the 3rd kind specified as lateral, angular external and internal corner elements. Each has one or more surfaces in contact with the environment and for which are valid the following expressions:

$$\lambda_{(x=x0,y)}\frac{\partial t_{(x=x0,y)}}{\partial x}=\alpha_{(x=x0,y)}\left(t_{(x=x0,y)}-t_{0(x=x0,y)}\right)$$
$$\lambda_{(x,y=y0)}\frac{\partial t_{(x,y=y0)}}{\partial y}=\alpha_{(x,y=y0)}\left(t_{(x,y=y0)}-t_{0(x,y=y0)}\right) \quad (5)$$

where:

$\alpha_{(x,y)}$ – local heat transfer coefficient near the surface, W/(m²·°C);

$t_{0(x,y)}$ – ambient temperature, °C.

Boundary conditions also depend on the geometric coordinates and therefore are nonlinear.

Since the process of phase transition occurs at a constant temperature must be set such power sources to the internal temperature at the boundary of the ice array maintained constant until the completion of phase transition:

$$q_{V(x,y)}=-\frac{\partial}{\partial x}\left(\lambda_{(x,y)}\frac{\partial t}{\partial x}\right)-\frac{\partial}{\partial y}\left(\lambda_{(x,y)}\frac{\partial t}{\partial y}\right) \quad (6)$$

Given the supply of heat from the external environment and knowing the specific heat crystallization (***r***) is possible determine the change in mass on the border of phase transition:

$$r_{(x,y)}\frac{dm_{(x,y)}}{d\tau}=\alpha_{(x,y)}\frac{\partial V}{\partial x}\left(t_{0(x,y)}-t_{\Pi(x,y)}\right)+\alpha_{(x,y)}\frac{\partial V}{\partial y}\left(t_{0(x,y)}-t_{\Pi(x,y)}\right) \quad (7)$$

where ∂V is elementary volume solid phase, m³.

To find the temperature distribution within the two-dimensional design planes parallel to divide it into a number of layers, using step Δx and Δy (Fig. 1). In order to be able to use grids with a lot of nodes will apply the "explicit" scheme in which each step for determining the temperature $t_{(i,j)}$ solved only one differential equation.

For internal structural elements (type 1), we assume that the mass volume, limited step $2\Delta x \cdot 2\Delta y$, concentrated in the central point of this element. Boundary elements (2,3,4,5) is located on the surfaces of the two-dimensional structures, so they concentrated only half the mass of the inner layers. External (6,7,8,9) and internal (10,11,12,13) in accordance with angular elements ¼ and ¾ mass internal element.

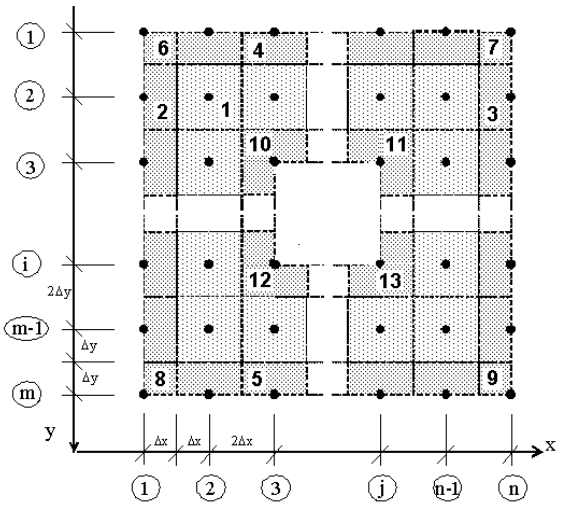

FIGURE 1. *Average two-dimensional design to domestic (1), marginal (2,3,4,5) and angular (6-13) elementary step of plane Δx and Δy*

Within each plot two-dimensional structures are uniformly distributed source the thermal (or heat loss) power q_v. For internal *i, j*-th element (type 1) differential equation of heat flows in finite differences can be written as:

$$c_{(i,j)}\rho_{(i,j)}\frac{\Delta t_{(i,j)}}{\Delta\tau}=\frac{1}{2\Delta x_{(i,j)}}\left(\frac{t_{(i,j-1)}-t_{(i,j)}}{\frac{\Delta x_{(i,j-1)}}{\lambda_{(i,j-1)}}+\frac{\Delta x_{(i,j)}}{\lambda_{(i,j)}}}-\frac{t_{(i,j)}-t_{(i,j+1)}}{\frac{\Delta x_{(i,j)}}{\lambda_{(i,j)}}+\frac{\Delta x_{(i,j+1)}}{\lambda_{(i,j+1)}}}\right)+\frac{1}{2\Delta y_{(i,j)}}*$$
$$*\left(\frac{t_{(i-1,j)}-t_{(i,j)}}{\frac{\Delta y_{(i-1,j)}}{\lambda_{(i-1,j)}}+\frac{\Delta y_{(i,j)}}{\lambda_{(i,j)}}}-\frac{t_{(i,j)}-t_{(i+1,j)}}{\frac{\Delta y_{(i,j)}}{\lambda_{(i,j)}}+\frac{\Delta y_{(i+1,j)}}{\lambda_{(i+1,j)}}}\right)+q_{v(i,j)} \quad (8)$$

where:

$c_{(i,j)}$ – heat capacity material enclosure, J/(kg·°C);

$\rho_{(i,j)}$ – density material heat accumulating platform, kg/m^3;

$t_{(i,j)}$ – temperature area of two-dimensional design with coordinates $X = i$, $Y = j$, °C;

$\Delta\tau$ – estimated time interval, s;

$\lambda_{(i,j)}$ – thermal conductivity material, W/(m°C);

Δx, Δy – coordinate steps according to the *X* axis and axis *H*, m;

$q_{V(i,j)}$ – specific volume heat source, W/m^3.

For two-dimensional problem of boundary conditions are different. First the number equal to the number of lines that limit the area calculation, both outside and inside the structure. Secondly, boundary conditions may vary along the axis for which they set. If an external surface area calculated to set the boundary conditions of the third kind, the heat balance equation for the first layer (item 2) would look like this:

$$c_{(i,j)}\rho_{(i,j)}\frac{\Delta t_{(i,j)}}{\Delta\tau}=\frac{1}{\Delta x_{(i,j)}}\left(\alpha_{(i,j)}\left(t_{o(i,j)}-t_{(i,j)}\right)-\frac{t_{(i,j)}-t_{(i,j+1)}}{\frac{\Delta x_{(i,j)}}{\lambda_{(i,j)}}+\frac{\Delta x_{(i,j+1)}}{\lambda_{(i,j+1)}}}\right)+\frac{1}{2\Delta y_{(i,j)}}*$$
$$*\left(\frac{t_{(i-1,j)}-t_{(i,j)}}{\frac{\Delta y_{(i-1,j)}}{\lambda_{(i-1,j)}}+\frac{\Delta y_{(i,j)}}{\lambda_{(i,j)}}}-\frac{t_{(i,j)}-t_{(i+1,j)}}{\frac{\Delta y_{(i,j)}}{\lambda_{(i,j)}}+\frac{\Delta y_{(i+1,j)}}{\lambda_{(i+1,j)}}}\right)+q_{v(i,j)} \quad (9)$$

where:

$\alpha_{(i,j)}$ – local heat transfer coefficient near of the corresponding element of the surface, W/(m^2°C);

$t_{o(i,j)}$ – ambient temperature, washing the local surface element, °C.

Similarly, we can write the boundary conditions (heat exchange with external air layers) for the other three sides of the rectangular area (Item 3, 4, 5 Fig. 1).

In linear boundary calculation on the plane and there are corner units, which are characteristic of simultaneous action boundary conditions on two coordinate axes. Corner units can be divided into "external" and "internal". External elements (type 6,7,8,9) only to touch the boundary element calculation plane Figure 1. Their thermal conditions can be described by equations of the form (type 6):

$$c_{(i,j)}\rho_{(i,j)}\frac{\Delta t_{(i,j)}}{\Delta\tau}=\frac{1}{\Delta x_{(i,j)}}\left(\alpha_{(i,j)}\left(t_{o(i,j)}-t_{(i,j)}\right)-\frac{t_{(i,j)}-t_{(i,j+1)}}{\frac{\Delta x_{(i,j)}}{\lambda_{(i,j)}}+\frac{\Delta x_{(i,j+1)}}{\lambda_{(i,j+1)}}}\right)+\frac{1}{\Delta y_{(i,j)}}*$$
$$*\left(\alpha_{(i,j)}\left(t_{o(i,j)}-t_{(i,j)}\right)-\frac{t_{(i,j)}-t_{(i+1,j)}}{\frac{\Delta y_{(i,j)}}{\lambda_{(i,j)}}+\frac{\Delta y_{(i+1,j)}}{\lambda_{(i+1,j)}}}\right)+q_{v(i,j)} \tag{10}$$

For providing any form of heat exchange area must take into account the internal components. These units will also be 4 types (10,11,12,13). The equations for describing heat exchange processes in such sites have the form (node 10):

$$c_{(i,j)}\rho_{(i,j)}\frac{\Delta t_{(i,j)}}{\Delta\tau}=\frac{1}{3\Delta x_{(i,j)}}\left(\frac{2\left(t_{(i,j-1)}-t_{(i,j)}\right)}{\frac{\Delta x_{(i,j-1)}}{\lambda_{(i,j-1)}}+\frac{\Delta x_{(i,j)}}{\lambda_{(i,j)}}}-\alpha_{(i,j)}\left(t_{(i,j)}-t_{o(i,j)}\right)-\frac{t_{(i,j)}-t_{(i,j+1)}}{\frac{\Delta x_{(i,j)}}{\lambda_{(i,j)}}+\frac{\Delta x_{(i,j+1)}}{\lambda_{(i,j+1)}}}\right)+\frac{1}{3\Delta y_{(i,j)}}*$$
$$*\left(\frac{2\left(t_{(i-1,j)}-t_{(i,j)}\right)}{\frac{\Delta y_{(i-1,j)}}{\lambda_{(i-1,j)}}+\frac{\Delta y_{(i,j)}}{\lambda_{(i,j)}}}-\alpha_{(i,j)}\left(t_{(i,j)}-t_{o(i,j)}\right)-\frac{t_{(i,j)}-t_{(i+1,j)}}{\frac{\Delta y_{(i,j)}}{\lambda_{(i,j)}}+\frac{\Delta y_{(i+1,j)}}{\lambda_{(i+1,j)}}}\right)+q_{v(i,j)}$$

(11)

Provided to the border $\frac{dt}{d\tau}=0$ value of the specific volume sources available for each boundary element on similar formulas:

$$q_{v(i,j)}=\frac{-1}{\Delta x_{(i,j)}}\left(\alpha\left(t_o-t_{(i,j)}\right)-\frac{t_{(i,j)}-t_{(i,j+1)}}{\frac{\Delta x_{(i,j)}}{\lambda_{(i,j)}}+\frac{\Delta x_{(i,j+1)}}{\lambda_{(i,j+1)}}}\right)+\frac{-1}{2\Delta y_{(i,j)}}*$$
$$*\left(\frac{t_{(i-1,j)}-t_{(i,j)}}{\frac{\Delta y_{(i-1,j)}}{\lambda_{(i-1,j)}}+\frac{\Delta y_{(i,j)}}{\lambda_{(i,j)}}}-\frac{t_{(i,j)}-t_{(i+1,j)}}{\frac{\Delta y_{(i,j)}}{\lambda_{(i,j)}}+\frac{\Delta y_{(i+1,j)}}{\lambda_{(i+1,j)}}}\right) \tag{12}$$

Moving boundary phase transition occurs discontinuously from one calculation to another node. The condition of the jump is the completion of phase transition in this node (eg. mass of ice in the node reached zero).

To increase the time step, this system of equations solved by means of convenient digital method of Runge-Kutta 4th order. Proposed mathematical model used to create a computer program in QBasic. Package size is 13 kilobytes. To test its efficiency calculation was performed decomposition of gas hydrate in the following initial data: initial temperature of methane hydrate -10°C; its thermal conductivity 0.5 W/(m°C); density 940 kg/m^3; heat transfer coefficient on the surface 23 W/(m^2°C); the heat of the phase transition 530000 J/kg; mass heat capacity hydrate-crystals 2060 J/(kg°C). Outdoor air temperature +20°C. coordinate step $\Delta x = \Delta y = 0.01$ m. The dimensions of a piece of gas hydrates in section 8*6 cm length 1 meter. On all four sides washed air. All Step 1 minute. The calculation results showed that the melting of the crystal-hydrate given shape, weighing 5.6 kg was completed for 10.4 days.

Conclusions

A mathematical model for calculating the decomposition of gas hydrates in equilibrium conditions. All thermal physical coefficients can be defined as a function of coordinates, temperature or temperature difference. In addition, its partitioning feature is the ability to design the desired number of layers, variable grid density and lack of rigid connection of coordinate and time steps.

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