Modeling the insulating properties of multicomponent solid foam-like material based on gel-forming systems

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Multicomponent solid foam-like material is proposed as an isolating agent for toxic and flammable liquids. The loss of fluidity of this material occurs due to gelation process. To increase the durability and isolating properties of the solid foam, an addition of water-soluble polymer carboxymethyl cellulose to the gel-forming system is proposed. The processes of vapor diffusion through a layer of fast-hardening foam on the surfaces of various liquids were modeled. The flow attenuation coefficient of fast-hardening foam was estimated for liquid vapors.

Keywords: mathematical model, fast-hardening foam, durability of foams, gel-forming system, vapor diffusion, flow attenuation coefficient.

Моделювання ізоляційних властивостей багатокомпонентного твердого піноподібного матеріалу на основі гелеутворюючих систем. *А.А.Кіреєв, І.К.Кириченко, Р.А.Петухов, А.Я.Шаршанов, Т.А.Ярхо*

Запропоновано в якості ізолюючого засобу для токсичних і горючих рідин використовувати багатокомпонентний твердий піноподібний матеріал, втрата текучості якого відбувається за рахунок процесу гелеутворення. Для збільшення стійкості та ізолюючих властивостей твердої піни до складу гелеутворюючої системи запропоновано вносити водорозчинний полімер — карбоксиметилцелюлозу. Проведено моделювання процесу дифузії парів рідин крізь шар швидкотвердіючої піни, нанесеної на поверхню рідин. Проведено оцінку значення коефіцієнта ослаблення потоку парів рідини швидкотвердіючою піною.

Предложено в качестве изолирующего средства для токсичных и горючих жидкостей использовать многокомпонентный твёрдый пенообразный материал, потеря текучести которого происходит за счет процесса гелеобразования. Для увеличения стойкости и изолирующих свойств твердой пены в состав гелеобразующей системы предложено вносить водорастворимый полимер — карбоксиметилцеллюлозу. Проведено моделирование процесса диффузии паров жидкостей сквозь слой быстротвердеющей пены, нанесенной на поверхность жидкостей. Проведена оценка значения коэффициента ослабления потока паров жидкости быстротвердеющей пеной.

1. Problem statement

Currently, about 6 million types of toxic substances are used for various industrial and household purposes worldwide, of which more than 500 belong to the group of extremely hazardous chemicals. They are potential sources of man-made disasters. Accidents in the places where such substances

are present can cause massive damage to people, farm animals and plants.

According to United Nations data, 350 large-scale chemical disasters occurred in the world over the past 30 years affecting about 100,000 people, more than 13,000 people died, and more than 3 million people were evacuated from the places of their residence. Nowadays, Ukraine is one of the most critical regions of Europe in terms of man-related environment burden exceeding the European average by 5–6 times.

A significant part of toxic substances are liquids. The turnover of some of them reaches thousands of tons (benzene, toluene, methanol, etc.) [1]. Accidental emergencies lead to the spillage of toxic liquids. At an initial stage of such accidents, the main danger is posed by liquid vapors. A number of methods are used to localize and eliminate such emergencies: installation of liquid curtains; vapor cloud scattering by gas-air stream; filling the spill with bulk adsorption materials; dilution of the spilled liquid with water or solutions of neutral substances; neutralization with solutions of chemically active reagents; cooling the spill with refrigerants; burning of the spill [2].

However, in most cases, the method of isolating the surface of the liquid with air-mechanical foams is used [3]. This method has a number of disadvantages, the main of which is the relatively rapid destruction of the foam as a result of exposure to various factors. The lifetime of foams does not exceed several tens of minutes. The process of localization and elimination of emergencies with the spill of toxic liquids lasts from several hours to several days. Therefore, the development of an insulating agent with a long service life is required.

As an alternative to air-mechanical foams, fast hardening foams (FHF) were proposed as an insulating agent with a long lifetime [4, 5].

For obtaining FHF, the processes of gel- and foam-formation are combined. In this case, the films of the foam cells represent a non-flowing system — a gel. The FHF destruction process differs from the corresponding process for air-mechanical foams. For the latter, destruction occurs mainly due to the gradual thinning of the foam films induced by water draining under an action of gravitational forces. In the FHF, destruction occurs due to evaporation of water from the gel layers leading to gel drying of and shrinkage of the gel layers followed by their cracking and spilling. The latter process is much slower than the process of liquid draining in foam films. The lifetime of such foams can be up to several days.

To increase further the lifetime of FHFs, addition of non-volatile hygroscopic liquids (glycerin, ethylene glycol) or water-soluble polymers (carboxymethyl cellulose (CMC), polyvinyl alcohol) was proposed. These foams were stable for several weeks [6]. This time is sufficient for liquidation of emergencies associated with the spill of toxic liquids. The insulating properties of such fast hardening, highly resistant foams were not experimentally investigated till now.

The existing models of gas diffusion through foams with closed cells were analyzed in [7]. In [7] also a model for calculating the diffusion coefficient based on the idea of the foam as a regular structure with cubic cells was proposed. To agree the calculated results with the experimental data, the adjustable geometric factor was introduced. In our work, in contrast to the previous ones, we propose to consider the diffusion of gas through the foam layer without demanding the regularity of the foam structure.

2. Problem statement and solution

The aim of this work was to model the process of transfer of liquid vapors through a layer of solidified foam without demanding the regularity of the foam structure, and to reveal the characteristics of this process.

The following assumptions were made during modeling:

— the film of the foam cell is a gel that has completely lost its fluidity;

— the gel framework retains an aqueous solution of some salts, foaming agent components and possibly contain water-soluble polymers;

— the relative contents of liquid and gaseous phases is expressed by the foam ratio (the ratio of the volume of the foam to the volume of the liquid from which the foam is formed).

The scheme of the analyzed situation is shown in Fig. 1. First of all, let us estimate the effective diffusion coefficient of liquid vapors through the foam. For this purpose, one should simplify the description of the process by averaging the values over the time interval $\Delta\tau$, which significantly exceeds as the characteristic time of diffusion of liquid vapors within the gaseous medium of one foam cell $\Delta\tau_a$, so the characteristic
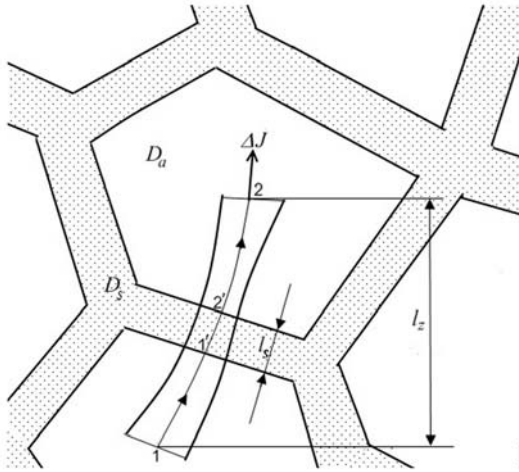
Fig. 1. Scheme of diffusion between adjacent cells. The numbers indicate the cross sections of typical stream tube. Symbols correspond to the boundaries between the inner space of the cells and the shell.

diffusion time through the shell of foam cell $\Delta\tau_s$. These characteristic times are given by the relations:

$$\Delta_a = \frac{l_a^2}{D_a}, s, \qquad (1)$$

$$\Delta_s = \frac{l_s^2}{D_s}, s, \qquad (2)$$

where D_a is the vapor diffusion coefficient inside the cell, m^2/s; l_a is the characteristic size of the cell, m; D_s is the vapor diffusion coefficient within the material of the foam cell shell, m^2/s; l_s is the foam cell shell thickness, m.

This averaging allows considering the process of vapor diffusion between the cavities of any two neighboring cells as quasi-stationary one. Using this fact we obtained a relationship between the concentration of vapors in neighboring cells and the diffusion fluxes of these vapors.

Fig. 1 shows a stream tube that bounds the diffusion flux ΔJ, $mol \cdot s^{-1}$, moving between the cross-sections with constant concentration values $c_1 = c(l_1)$ and $c_2 = c(l_2)$, $mol \cdot m^{-3}$, (l is a distance counted from 1 to 2 along the stream tube). Fick's law in this case has the form:

$$\Delta J = -D(l) \cdot \frac{\partial c}{\partial l} \cdot \Delta F(l), \qquad (3)$$

where $D(l)$ and $\Delta F(l)$ are the diffusion coefficient and cross-sectional area of equal concentrations of the stream tube at a distance l.

Equation (3) can be re-written as

$$\frac{\partial c}{\partial l} = -\frac{\Delta J}{D(l) \cdot \Delta F(l)} \qquad (4)$$

and integrated in three intervals of concentration continuity c: from 1 to 1′, from 1′ to 2′, and 2′ from to 2 (Fig. 1). Taken into account that ΔJ is constant in stationary mode, assuming that the diffusion coefficient is invariable $D(l)$ within each of the spatial intervals, we get:

$$c_1 - c(l_{1'} - 0) = \frac{\Delta J}{D_a} \cdot \int_1^{1'} \frac{dl}{\Delta F(l)}, \qquad (5)$$

$$c(l_{1'} + 0) - c(l_{2'} - 0) = \frac{\Delta J}{D_a} \cdot \int_{1'}^{2'} \frac{dl}{\Delta F(l)}, \qquad (6)$$

$$c(l_{2'} + 0) - c_2 = \frac{\Delta J}{D_a} \cdot \int_{2'}^{2} \frac{dl}{\Delta F(l)}. \qquad (7)$$

Let us take into account that at the boundaries (1′ and 2′), the connection between the concentrations in the contacting media is satisfied:

$$c(l_{1'} + 0) = \frac{c(l_{1'} - 0)}{k_1}, \qquad (8)$$
$$c(l_{2'} - 0) = \frac{c(l_{2'} + 0)}{k_2},$$

where k_1, k_2 are distribution coefficients at corresponding borders. As the film between the cells is thermally thin, and therefore the temperatures at the boundaries of the film are practically the same, then

$$k_1 = k_2 = k, \qquad (9)$$

As a result, the consideration of the system of equations (5)–(9) gives a relationship between the diffusion flux and the vapor concentrations inside neighboring cells:

$$\Delta J = \frac{c_1 - c_2}{\frac{k}{D_s}\int_{1'}^{2'}\frac{dl}{\Delta F(l)} + \frac{1}{D_a}\left[\int_1^{1'}\frac{dl}{\Delta F(l)} + \int_{2'}^{2}\frac{dl}{\Delta F(l)}\right]}. \qquad (10)$$
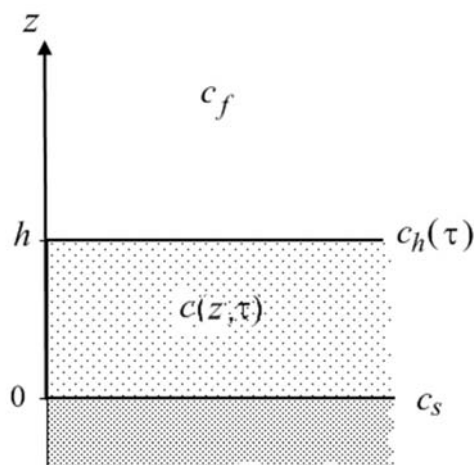
Fig. 2. Geometry of the problem of vapor diffusion through a flat foam layer (liquid ($z <$ 0) is separated from external space ($z > h$) by the layer of foam ($0 < z < h$)).

Further, we note that in all practical situations:

$$D_a \frac{l_s}{l_a} >> \frac{D_s}{K} , \qquad (11)$$

allowing us to retain only the first term in the denominator of (10). As a result, relation (10) takes the form:

$$\Delta J = \frac{D_s}{k} \cdot \frac{c_1 - c_2}{l_s} \cdot \Delta F(l'), \qquad (12)$$

where $l_s = l_{2'} - l_{1'}$ is a film thickness; $\Delta F(l')$ is an average value of the cross-sectional area of the stream tube within the film, m^2.

Re-writing (12) using l_z that is the displacement in the general direction of diffusion during the passage of the current tube (Fig. 1, which implies the total transfer in the vertical direction), we get the expression:

$$\Delta J = \left[\frac{D_s}{k} \cdot \frac{l_z}{l_s} \right]_s \cdot \frac{c_1 - c_2}{l_z} \cdot \Delta F(l'). \qquad (13)$$

Comparing (3) and (13), we find that the expression in square brackets in (13) plays the role of the diffusion coefficient of liquid vapors over the cavities of the foam cells in a given direction. For such a process, the effective diffusion coefficient can be estimated by:

$$D_{ef} = \frac{D_s}{k} \cdot \frac{\overline{l_z}}{l_s}, \qquad (14)$$

where $\overline{l_z}$ is the mean value of the projection of the length of the stream tube between two adjacent cells on the general direction of diffusion.

l_z is of the order of the average size of foam cells in the direction of diffusion l_a, but does not exceed it. It depends on the geometric structure of the foam. l_z is defined easily only for foams with a simple symmetrical structure. So, if the foam cells are identical parallelepipeds, all faces of which completely coincide with the corresponding faces of neighboring cells, and the direction of diffusion coincides with the direction of one of the main axes of the parallelepiped, then l_z is equal to the length of an edge parallel to this axis. This circumstance means diffusion anisotropy in such anisotropic foam.

Relation l_a / l_s directly depends on the expansion rate of the foam k_f and its shape. At $k_f >> 1$ the dependence has the form:

$$\frac{l_a}{l_s} = K_F \cdot k_f, \qquad (15)$$

in which the dimensionless factor $K_F > 1$ (form-factor) is determined exclusively by the shape of the foam cells. So in the case of foam with cells in the form of identical cubes $KIVF = 3$.

For the foam considered as a homogeneous medium, the concentration of vapors $c(z, \tau)$, related to gas regions inside a flat layer of such foam, satisfies the equation of nonstationary diffusion

$$\frac{\partial c}{\partial \tau} = D_{ef} \cdot \frac{\partial^2 c}{\partial z^2}, \qquad (16)$$

where z is a coordinate directed normal to the flat foam layer measured from the border of the foam layer with the insulated liquid (Fig. 2), τ is the time counted from the start of the diffusion process.

The boundary condition to (16) is the given concentration of liquid vapors at the liquid-foam interface equal to the concentration of saturated vapors c, mol·m^3:

$$c(0, \tau) = c_s, \qquad (17)$$

and the given conditions of mass transfer at the border of the foam with the external space:

$$-D_{ef} \cdot \frac{\partial c(z, \tau)}{\partial z}\Big|_{z=h-0} = \beta \cdot [c(h, \tau) - c_f], \qquad (18)$$

where c_f is vapor concentration in external space, mol·m^{-3}.

Mass transfer coefficient β, m·s^{-1}; is determined using the equations of the similarity theory [8]. It is equal to:

$$\beta = Nu_D \cdot \frac{D_a}{L}, \qquad (19)$$

where L is the characteristic size of the flow around the foam surface, m (as a rule, by the order of magnitude L coincides with the characteristic size of the foam surface). Diffusion Nusselt criterion Nu_D (similar to Sherwood criterion Sh) depends on the conditions of the external flow of the medium around the foam surface. It can be expressed through the Reynolds and Schmidt criteria using the criterial equations of mass transfer obtained from experiments and included to reference materials.

As an initial condition of the diffusion problem it is naturally to take the homogeneous initial distribution of the vapor concentration in the foam c_0:

$$c(z,0) = c_0, \quad 0 < z < h, \qquad (20)$$

An analytical solution to the problem (16)–(18), (20) for the case of concentration independence of the coefficients is known. An explicit form of such a solution in the case of the heat conduction problem is given in [9]. In dimensionless variables this solution for the vapor concentration $c_h = c(h, \tau)$ on the outer surface of the foam layer gives:

$$\theta_h(Fo_d, Bi_D, \theta_f) = \frac{1 + Bi_D \cdot \theta_f}{1 + Bi_D} + \qquad (21)$$

$$+ 2 \cdot \sum_{n=1}^{\infty} A_n(Bi_D, \theta_f) \cdot \exp(-\mu_n^2 \cdot Fo_D),$$

where θ_h and θ_f denote relative excess concentrations:

$$\theta_h \equiv \frac{c_h - c_0}{c_s - c_0}, \quad \theta_f \equiv \frac{c_f - c_0}{c_s - c_0}. \qquad (22)$$

Parameter

$$Fo_D \equiv \frac{\tau}{\tau_D} = \frac{D_{ef} \cdot \tau}{h_2}, \qquad (23)$$

which is the dimensionless time of the diffusion process, is called the diffusion Fourier criterion. It is associated with the

characteristic diffusion time through the foam layer

$$\tau_D \equiv \frac{h^2}{D_{ef}}, s. \qquad (24)$$

Another dimensionless parameter

$$Bi_D \equiv \frac{\beta \cdot h}{D_{ef}}, \qquad (25)$$

which is the dimensionless coefficient of mass transfer, is called the Biot diffusion criterion. We should note that according to the relations (14) and (19)

$$Bi_D = Nu_D \cdot k \cdot \frac{D_a}{D_s} \cdot \frac{l_s}{\overline{l}_z} \cdot \frac{h}{L}. \qquad (26)$$

The coefficients of series (21) are described by

$$A_n(Bi_D, \theta_f) = \frac{1 - \cos(\mu_n) \cdot \theta_f}{\left(Bi_D + 1 + \dfrac{\mu_n^2}{Bi_D}\right) \cdot \cos(\mu_n)}. \qquad (27)$$

In which μ_n denotes the nth root of the characteristic equation

$$\mathrm{tg}(\mu) = -\frac{\mu}{Bi_D}. \qquad (28)$$

One should note that the values $\mu_n(Bi_D)$ are within following intervals

$$(n - 0.5) \cdot \pi < \mu_n < n \cdot \pi, \quad n=1,2,3,,,,. \qquad (29)$$

The first term in relation (21) gives the stationary value of the relative excess concentration $c_{h.ct}$. According to (21) and definitions (22) and (25), we obtain:

$$c_{h.st} = \frac{c_s + Bi_D \cdot c_f}{1 + Bi_D} = \frac{c_s \cdot \dfrac{1}{\beta} + c_f \cdot \dfrac{h}{D_{ef}}}{\dfrac{1}{\beta} + \dfrac{h}{D_{ef}}} =$$

$$= \frac{c_s \cdot \dfrac{L}{Nu_D \cdot D_a} + c_f \cdot \dfrac{h}{D_{ef}}}{\dfrac{L}{Nu_D \cdot D_a} + \dfrac{h}{D_{ef}}}. \qquad (30)$$

It should be noted that for $Fo_D \ll 1$ the series (21) converges poorly. From general considerations, it is clear that for $Fo_D = 0$, $\theta_h = 0$. The calculations (at $Bi_D = 1$ and $c_f = c_0$) have shown that at $Fo_D = 0$ for obtaining $\theta_h < 0.01$ it is necessary to take into account 32 terms of the series. At $Fo_D = 0.01$ to obtain an absolute discrepancy (be-

tween the exact solution and a partial sum) less than 0.01, 6 terms must be taken into account. The absolute discrepancy (between the exact solution and the partial sum) less than 0.01 is provided by 2 terms of the series at $Fo_D > 0.16$. In this case, dependence (21) takes the form

$$\theta_h(Fo_D, 1.0) = 0.5 + \frac{2 \cdot \exp(-\mu_1^2 \cdot Fo_D)}{(2 + \mu_1^2) \cdot \cos(\mu_1)}, \quad (31)$$

where $\mu_1(Bi_D) = \mu_1(1) = 2.0288$.

Using the results obtained we can evaluate the insulating properties of the fast-hardening foam obtained using the gel-forming system $Na_2O \cdot nSiO_2$ (9 %) + $NaHCO_3$ (9 %) + CMC (0.5 %) + "Morskoy" foaming agent (6 %) with respect to benzene vapors. We took reference data on the characteristics of benzene and experimental data on the characteristics of the gel-like layer (all data for $t = 20°C$):

c_w is the benzene solubility in water, $22.8 \cdot 10^{-3}$ mol/l [10];

ρ_w is the average density of gelling solutions, 1007 kg/m³;

ν_w is the viscosity of 0.5 % CMC solution, $31,9 \cdot 10^{-6}$ m²/s;

c_s is the concentration of benzene saturated vapors in air, $4.10 \cdot 10^{-3}$ mol/l;

D_a is the benzene diffusion coefficient in air, $7.8 \cdot 10^{-6}$ m²/s;

r_0 is the effective radius of a benzene molecule (gas kinetic radius), $r_0 = 5.27 \cdot 10^{10}$ m.

According to the definition (8) $k = c_s/c_w = 0.18$. Diffusion coefficient D_s will be estimated by the formula for the diffusion coefficient of a Brownian particle (benzene molecule) in liquid:

$$D_s = \frac{k_B \cdot T}{6 \cdot \pi \cdot \rho_w \cdot \nu_w \cdot r_w} = \quad (32)$$
$$= 1.27 \cdot 10^{-11}, \, m^2 \cdot s^{-1},$$

where $k_B = 1.38 \cdot 10^{-23}$ J·K⁻¹ is Boltzmann constant; $T = 293$ K.

For further estimations, we will take the following values: foam expansion $k_f = 10$; form-factor $K_f = 3$ (15); foam cell size $l_a = 1 \cdot 10^{-3}$ m; $\overline{l}_z = l_a$. According to this we get:

— from (15) $l_s = 3.3 \cdot 10^{-5}$ m and $l_a/l_s = 30$;

— from (14) $D_{ef} = 2.1 \cdot 10^{-9}$ m²·s⁻¹;

— from (1) $\Delta\tau_a = 0.13$ s;

— from (2) $\Delta\tau_s = 86$ s.

For further evaluation, we take the thickness of the foam layer $h = 1 \cdot 10^{-2}$ m. So, according to (24), the characteristic diffusion time through such a layer is $\tau_D = 4.7 \cdot 10^4$ s ≈ 13 h.

One should note that according to (26) $Bi_D = 3.6 \cdot 10^3 \cdot Nu_D \cdot h/L$, that at $h = 1 \cdot 10^{-2}$ m gives $Bi_D = 36 \cdot Nu_D/L$. Taking into account that $Nu_D \geq 1$, we get that in most cases of using such a foam, $Bi_D >> 1$. It is important in assessing the protective properties of the foam, since the attenuation coefficient of the benzene flux by the protective coating K equal to the ratio of the flow from free surface to the flow through the protective layer, cannot be less than its stationary value $K_{st} = 1 + Bi_D$. It should be noted that in the example under consideration for $Nu_D = 1$ and $L = 1$ m the estimation gives the value of the flow attenuation coefficient $K_{st} = 37$.

Comparison of the insulating properties of fast-hardening foam and insulating agents based on silicates [11, 12] allows us to conclude that it is not worse, and also has an advantage over them in easier application to the liquid layer.

3. Conclusions

As a result of modeling the process of gas diffusion through the foam layer it was shown that, as in regular structures, the effective diffusion coefficient contains the form-factor, which is determined exclusively by the foam geometry.

Fast hardening foam with a layer thickness of 1 cm is an effective insulating agent even in stationary conditions.

The proposed insulating agent is close in insulating properties to the previously proposed silicate-based insulating materials, however, it has an advantage in easier application to the liquid layer.

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