

Experimental Study of the Insulating Properties of a Lightweight Material Based on Fast-Hardening Highly Resistant Foams in Relation to Vapors of Toxic Organic Fluids

PIETUKHOV Ruslan^{1,a*}, KIREEV Alexander^{1,b}, TREGUBOV Dmytro^{1,c},
HOVALENKOV Serhii^{1,d}

¹National University of Civil Defence of Ukraine, 94, Chernishevskya str., Kharkov, Ukraine, 61023

^aruslan.petuxov@gmail.com, ^b53kireev@gmail.com, ^ccxxtregubov1970@nuczu.edu.ua,
^egovalenkov@ukr.net.

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Abstract. To isolate the surface of toxic liquids, it is proposed to use fast-hardening highly resistant foams. To obtain fast-hardening, highly resistant foams, the process of gel and foaming is combined. For this, solutions of sodium polysilicate and gelation catalyst are mixed. To increase the stability of the foams, it is proposed to add water-soluble polymers to the gel-forming composition. It is shown that a fast-hardening foam of the composition $\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (9%)+ NaHCO_3 (9%)+6% foaming agent +0.5% carboxymethyl cellulose with thickness 5 cm reduces the mass rate of benzene evaporation by more than 5 times. It retains its insulating properties for more than 5 days. It is concluded that it is advisable to use fast-hardening highly resistant foams for the elimination of emergencies with the spill of toxic liquids.

Introduction

Currently, about 6 million toxic substances are used in the world for various industrial and household purposes, many of them belong to the group of extremely hazardous chemicals. A significant part of toxic substances are liquids. Some of them have a turnover of thousands of tons [1]. Periodically Emergencies occur, which lead to the spill of toxic liquids. At the initial stage of such accidents, the main hazard is represented by liquid vapors. They can poison people and have a negative impact on flora and fauna.

To reduce the negative consequences of such accidents, a number of methods are used: installation of liquid curtains; scattering and displacement of a vapor cloud by a gas-air flow; backfilling of the spill and absorption of liquid by bulk adsorption materials; dilution of liquid spillage with water or solutions of neutral substances; neutralization with solutions of chemically active reagents; cooling the spill with refrigerants; burning of the strait [2]. However, in most cases, the method of isolating the surface of the liquid with air-mechanical foams is used [3]. This method has several disadvantages, the main one being the rapid destruction of the foam. The durability of the foams does not exceed several tens of minutes. The process of liquidation of emergencies with the spill of toxic liquids lasts from several hours to several days. Therefore, it is relevant to develop an insulating agent with high insulating properties and a long time to maintain performance.

Main part

As an alternative to air - mechanical foams, as an insulating agent with a long lifetime, it has been proposed to use the fast hardening foams (FHF) [4]. Upon receipt of the FHF, two sequential processes are carried out. Initially, two components of the gelling system (GS) are mixed - a solution of a gelling agent and a solution of a gelation catalyst. In this case, both components of GS contain a foaming agent (FA) in an amount of 6 wt%. Subsequently, the resulting composition is foamed using one of the existing methods. Then the foam is applied to the surface of the spilled liquid. The applied foam is retained on the surface of the liquid and after a while hardens due to the

completion of the gelation process. In this case, the films of foam cells are a non-flowing system - a gel.

The time of the operations of mixing the GS components, foaming the composition and feeding the foam should be less than the time of the gel's flow loss. The time of loss of fluidity of the gel is regulated by changing the concentrations of the GS components. In all cases, it was previously proposed to use liquid glass as a gelling agent, which is a concentrated aqueous solution of sodium polysilicates ($\text{Na}_2\text{O} \cdot n\text{SiO}_2$) [5]. 34 previously studied systems were considered as catalysts for gelation [6]. In addition to these systems, systems with the following gelation catalysts were studied: K_2CO_3 , NaHCO_3 , NaH_2PO_4 . Out of 37 GS, acceptable results for gelation times were shown by systems with the following gelation catalysts, acid salts KH_2PO_4 , NaHCO_3 , NaH_2PO_4 , as well as a number of ammonium salts – $(\text{NH}_4)\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$. The time limit for pour point was chosen as a minimum of 30 seconds. This time is enough to carry out operations, starting with mixing the components of GS and ending with the supply of foam to the surface of the liquid. For the longest time of foam flow loss was taken 120 seconds. During this time, the non-hardened foam is destroyed to a small extent.

For selected GS, the concentration of water glass can vary in the range (3–12) wt.%, And the concentration of gelation catalysts (3.5–15) wt.%. Preliminary studies have shown that after the loss of fluidity, the foams gradually collapsed. Visual observation of the processes of destruction of air-mechanical foam and FHF made it possible to establish that the processes of their destruction are significantly different. For air-mechanical foam, destruction occurs mainly due to the gradual thinning of the foam films and due to the drainage of water under the action of gravitational forces. In FHF, destruction occurs due to the evaporation of water from the gel layers. This leads to drying of the gel and shrinkage of the gel layers, which leads to their gradual cracking and sprinkling. The latter process is much slower than the process of liquid draining from foam films. The time for the complete destruction of such foams reaches several days. The results of work on the stability of a number of FHF s are presented in the publication [7].

To select the system with the longest foam destruction time, it is necessary to additionally investigate systems with such gelation catalysts: KH_2PO_4 , NaH_2PO_4 , $(\text{NH}_4)_2\text{HPO}_4$, $(\text{NH}_4)_2\text{SO}_4$. In addition to determining the destruction time of the FHF, it is necessary to study the insulating properties of solid foams and the effect on it of the thickness of the foam layer.

Problem statement and solution. The aim of this work is to experimentally study the stability of foams and their insulating properties in relation to vapors of toxic organic liquids. Benzene (C_6H_6) was chosen as such a liquid. It is widely used in industry. Benzene belongs to the class of highly hazardous substances (second hazard class) [8]. It has a noticeable volatility, can cause acute and chronic poisoning. Due to its low solubility in water, such methods of reducing its concentration in the air as setting up water curtains, diluting a liquid spill with water or solutions of neutral substances are ineffective.

Materials and Equipment.

We used benzene containing less than 0.4% impurities. Its purity was checked by density and refractive index. Liquid glass (LG) used in the work contained 1.3% sodium polysilicate (density 1.31 g/cm^3 , silicate modulus 2.5). Solutions of liquid sodium glass were prepared by the dilution method.

Carboxymethyl cellulose - sodium salt was used with a degree of polymerization of 1000 and a degree of substitution for carboxymethyl groups of 90–95. Polyvinyl alcohol had the following physicochemical properties - the degree of polymerization is 1200, the degree of hydrolysis is 88%, and the crystallinity is 30%. Glycerin had the following physicochemical characteristics - density 1.260 g/cm^3 , mass fraction of the main substance not less than 99%. The salts used as catalysts for gelation contained at least 99.5% of the basic substance. Salt solutions were prepared by the gravimetric method. Their concentration was controlled by density using the areometric method. To determine the mass of substances, we used a THB-600 weighing-machine with a weighing accuracy of $\pm 0.01 \text{ g}$.

Study of the Stability of Foams.

The experimental procedure for determining the stability of the foam is given in [7]. At the same time, the dependences of the height of the FHF layer on time were studied. The studies were carried out at ambient temperature (18 ± 3) °C. Figure 1 shows the time dependences of the change in the foam layer thickness for systems with the longest foam destruction time ($\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (9 mac.%) + NaHCO_3 (9%) – system 1), ($\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (6 wt%) + $(\text{NH}_4)\text{H}_2\text{PO}_4$ (7%) – system 2) and ($\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (6 wt%) + $(\text{NH}_4)_2\text{CO}_3$ (16%) (system 3). the dependence for the system with the lowest concentrations of GS components ($\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (4.5 wt.%) + NH_4Cl (4.1 wt.%) – (system 4) is shown. In all cases, the concentration of the foaming agent (FA) "Sea" in solutions was 6 wt%

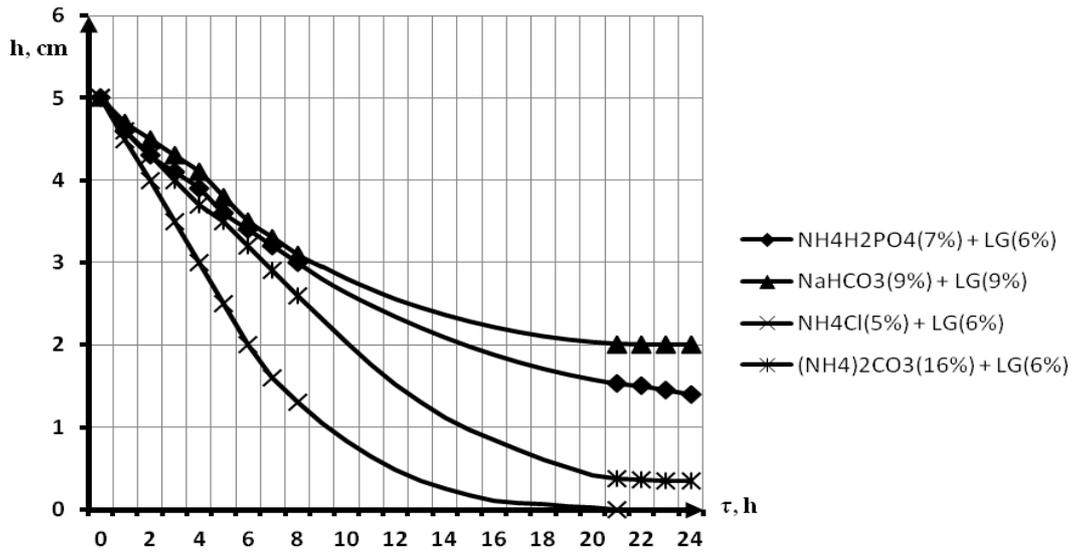


Fig. 1. A graphical representation of the change in the FHF layer thickness (h , cm) in time (τ , h) for systems 1, 2 3 and 4

Analysis of the results obtained allows us to conclude that the slowest destruction of foam is for the system ($\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (9 wt.%) + NaHCO_3 (9%) + 6% FA). For this system, the dynamics of foam destruction was studied for different layer thicknesses. The corresponding results are shown in Fig. 2.

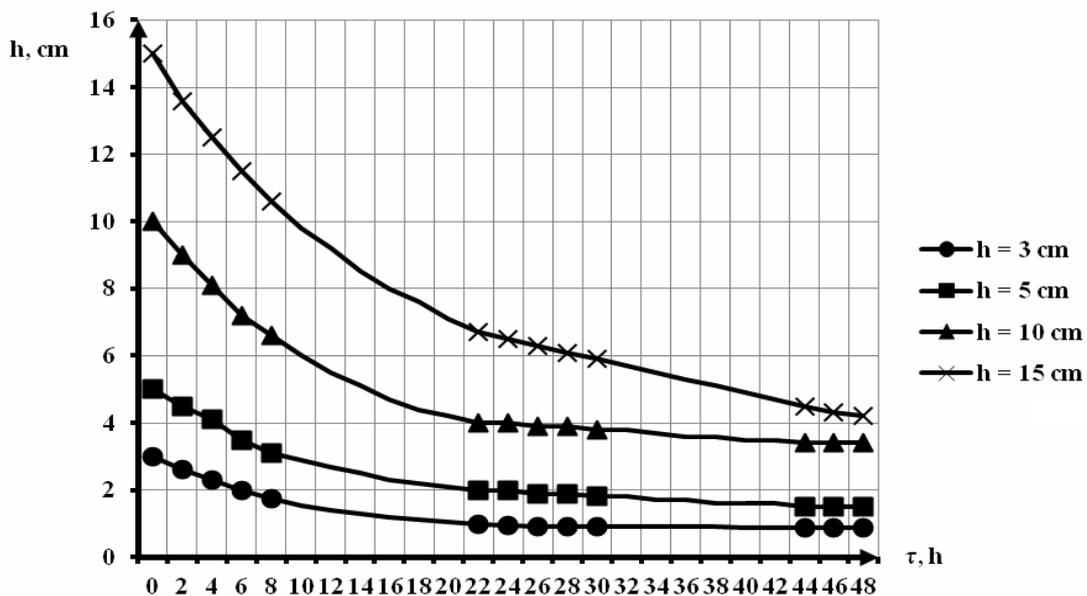


Fig. 2. A graphical representation of the change in the FHF layer thickness (h , cm) in time (τ , h) for system 1

Analysis of these results allows us to conclude that in 48 hours the thickness of the FHF layer decreases by $(65 \pm 5)\%$. By visual observations, it was found that after 24 hours, even for a FHF thickness of 15 cm, cracks appear in the foam, which after 48 hours reach the surface on which the foam is applied. This indicates that the insulating properties of FHF ($\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (9 wt.%) + NaHCO_3 (9%) + 6% FA) will significantly decrease after 24 hours. It should be noted here that air-mechanical foam is completely destroyed in 1–1.5 hours. That is, FHF has a lifetime advantage over air-mechanical foam by more than 10 times. However, 24 hours may not be enough for the complete elimination of an emergency related to a toxic liquid spill.

To further increase the lifetime of FHF s, it was proposed to introduce into their composition low-volatility hygroscopic liquids (glycerin (GC), ethylene glycol (EG)) or water-soluble polymers (carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA)). FHF systems $\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (9 wt.%) + NaHCO_3 (9%) + 6% FA + 0.5% CMC showed high resistance. [9]. After 72 hours, only shallow cracks form on this foam. Subsequently, in the absence of external influences, the foams remained unchanged for a month.

In this work, according to the methodology given in [9]. the resistance of the FHF systems $\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (9 wt.%) + NaHCO_3 (9%) + 6% FA + GC (system 5) and $\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (9 wt.%) + NaHCO_3 (9 %) + 6% FA + PVA (system 6). In this case, the concentration of GC varied in the range (2–20)%, and the concentration of PVA (0.5–2)%.

Initially, the multiplicities of the obtained foams were determined (K):

$$K = V_f/V_1, \quad (2)$$

where V_f is the volume of the foam, V_1 is the volume of the liquid from which the foam is obtained.

The results of experiments to determine the expansion rate of the foam showed the following results. For system 5, the foam ratio varied from 12 at a GC content of 2% to 5 at a GC content of 20%. In the case of system 6, with an increase in the PVA content from 0.5% to 2%, the foam expansion decreased from 7 to 2. The time of the appearance of the first deep cracks for systems 5 and 6 increased with an increase in the content of GC and PVA. The corresponding data, together with the previously obtained results [7], are presented in tables 1–3.

Table 1. Characteristics of fast- hardening foam for the CMC system

	Mass fraction of CMC in FHF, ω , (%)				
	0	0.5	1	1.5	2
K	14	6	3	< 2	< 2
τ_1 , (hours)	5	16	20	26	32
τ_2 , (hours)	8	30	24	31	37
τ_3 , (hours)	15	96	48	42	40
D, (%)	30	<1	5	10	15

where K is the foam ratio; τ_1 is the time of appearance of the first signs of destruction of the surface layer of the foam; τ_2 is the time of the appearance of shallow cracks at the surface layer of the foam; τ_3 is the time of the appearance of the first cracks to the entire depth; D - fraction of open surface at the final stage of destruction.

As can be seen from the data presented, FHF's containing glycerol (system 5) showed the highest stability. However, a high stability of such foam was achieved at high glycerol contents. In addition, when studying the buoyancy of these foams in a number of organic fluids, they showed a negative result. Due to the low expansion of the foam and the higher density of glycerin, such foams gradually melted. Comparison of the characteristics of foams with the content of CMC and PVA, the former showed great stability. The best results were shown by the FHF of the system $\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (9 wt.%) + NaHCO_3 (9%) + FA (6%) + CMC (0.5%). Fig. 3 – Fig. 5 show an illustration of the change in the appearance of the FHF over time for this system.

Table 2. Characteristics of fast-hardening foam for the GC system

	Mass fraction of GC in FHF ω , (%)				
	2	5	10	15	20
K	12	10	8	6	5
τ_1 , (hours)	6	8	10	21	32
τ_2 , (hours)	8	10	22	32	37
τ_3 , (hours)	11	22	*	*	*
D, (%)	25	20	*	*	*

* during the experiments, cracks did not appear to the full depth

Table 3. Characteristics of fast-hardening foam for the PVA system

	Mass fraction of PVA in FHF ω , (%)			
	0.5	1	1.5	2
K	7	4	3	< 2
τ_1 , (hours)	12	20	24	30
τ_2 , (hours)	24	20	28	34
τ_3 , (hours)	72	48	48	42
D, (%)	10	20	30	30

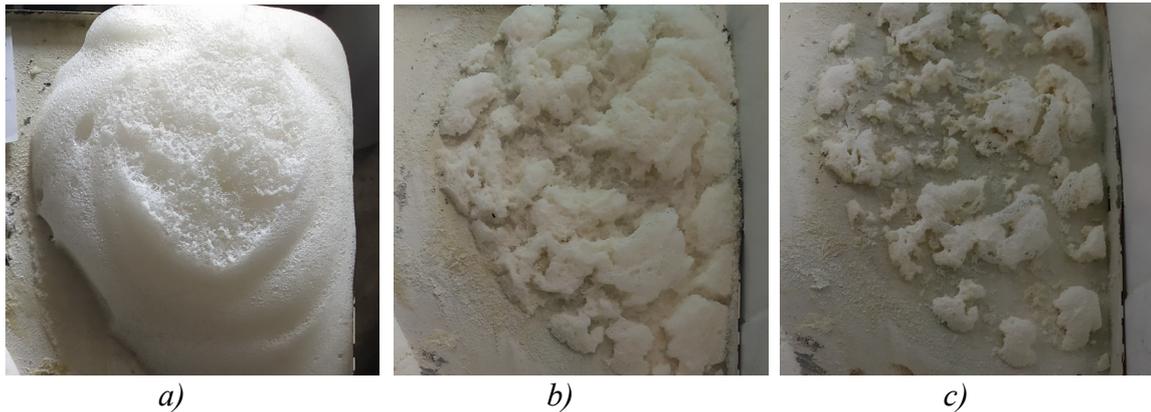


Fig. 3. External view of FHF (system 1 without CMC): a) FHF initial view; b) FHF after 24 hours; c) FHF after 72 hours

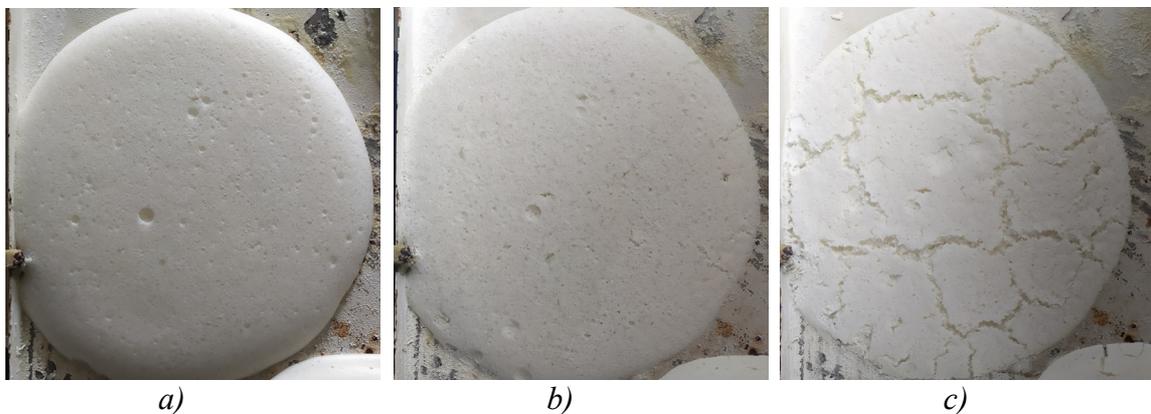


Fig. 4. External view of FHF (system 1 + 0.5% CMC): a) FHF initial view; b) FHF after 24 hours; c) FHF after 72 hours

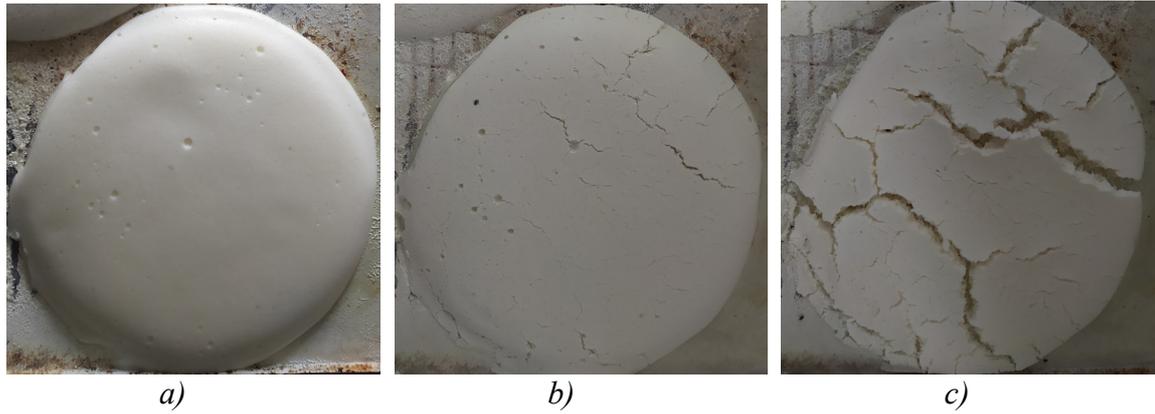


Fig. 5. External view of FHF (system 1 + 1% CMC): a) FHF initial view; b) FHF after 24 hours; c) FHF after 72 hours

As can be seen from the given data, the FHF on a solid surface retains its integrity for up to 4 days.

Investigation of the buoyancy and stability of FHF applied to the surface of benzene

In addition to the resistance of the FHF on a solid surface, it is necessary to establish the buoyancy and resistance of the FHF layer on the surface of the toxic liquid. Benzene was chosen as such a liquid. As a quantitative characteristic of the buoyancy of the FHF (F), as in [10], the ratio of the height of the foam glass (FG) layer located above the liquid level to the total height of the FG layer was chosen:

$$\Pi = \frac{h \uparrow}{h} = \frac{h \uparrow}{h \uparrow + h \downarrow}, \quad (3)$$

where $h \uparrow$ is the height of the FHF layer above the liquid layer; h is the total thickness of the FHF layer; $h \downarrow$ is the height of the FHF layer below the liquid level. Investigations of the behavior of FHF deposited on a benzene layer were carried out in glass containers. The layer heights were determined visually. The corresponding data are presented in table 4.

Table 4. The release time of benzene on the upper surface of the FHF (τ), the buoyancy of fast hardening foams immediately after application to the surface of benzene (P0), after 1, 6 and 24 hours after application (P0, P1, P6, P24), for systems:

- 1 – $\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (9 wt%)+ NaHCO_3 (9%)+6% FA + 0.5% CMC,
- 2 – $\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (9 wt%) + NaHCO_3 (9%) + 6% FA + 20% GC,
- 3 – $\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (9 wt%) + NaHCO_3 (9%) + 6% FA + 1% PVA

system	P ₀ ,	P ₁	P ₆	P ₂₄	τ , (hours)
1	85	65	40	35	>48
2	60	40	0	0	2
3	80	60	40	30	30

Based on the above data, it can be concluded that foams gradually melt on the surface of benzene. This is due to the gradual filling of the foam cells at the bottom of the solid foam. In this case, the helium framework itself retains its integrity, and the foam films formed by the liquid lose their continuity. Of the FHF's studied on the surface of liquid benzene, the most stable foam is based on the system $\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (9%)+ NaHCO_3 (9%) + 6% FA + 0.5% CMC. After 24 hours, this foam is immersed in the benzene layer at 65% of its height, which corresponds to a buoyancy of 35%. The time it takes for benzene to reach the surface of the foam is at least 48 hours. With a small thickness

of the benzene layer, after a while the foam comes into contact with the hard bottom and then retains its integrity for up to 5 days.

Insulating Properties of a Layer of Fast- Hardening Foam

To investigate the insulating properties of fast-hardening foam, was chosen the FHF which showed the highest resistance – $\text{Na}_2\text{O}\cdot 2.5\text{SiO}_2(9\%)+\text{NaHCO}_3(9\%) + 6\% \text{FA} + 0.5\% \text{CMC}$, as well as this system without the addition of CMC. The gravimetric method was chosen as the research method. Benzene was chosen as the toxic liquid. Initially, the rate of evaporation of benzene from a free surface was investigated. For this, 0.3 liters of benzene was poured into a cylindrical container with a capacity of 0.5 liters. After that, the container was installed on a THB-600 electronic continuous weighing-machine and the weight loss of benzene was determined for each minute. The dependence of the weight loss of benzene turned out to be close to linear, which indicated the rapid establishment of a stationary mode of the benzene evaporation process. The measurements were taken for 20 minutes. The air temperature was $(20 \pm 1)^\circ\text{C}$. Based on the data obtained, the mass rate of evaporation of benzene (V) from the free surface was calculated by the ratio:

$$V = \frac{\Delta m}{\tau \cdot S}, \quad (4)$$

where Δm is the change in the mass of the liquid as a result of its evaporation; τ - time of liquid evaporation; S is the surface area of the liquid;

The studies were carried out three times and determined the average result. The mass rate of evaporation of benzene from the free surface was $0.97 \cdot 10^{-2} \text{ g}/(\text{sec} \cdot \text{m}^2)$. Further, studies were carried out on the insulating properties of FHF in relation to benzene vapors. To do this, they took a metal mesh with a diameter equal to the diameter of the container and a side height of 5 cm, put it on a container with benzene and fed it with a FHF, so that the side height without foam was zero. Then, a container with a grid filled with FHF was placed on an weighing-machine and the loss of benzene mass through the FHF layer was recorded after 20 minutes. For this, the foam mesh was removed from the metal container. After that, the mass evaporation rate of benzene was calculated, which was $0.23 \cdot 10^{-2} \text{ g}/(\text{sec} \cdot \text{m}^2)$ for FHF without CMC and $0.1 \cdot 10^{-2} \text{ g}/(\text{sec} \cdot \text{m}^2)$ with the addition of 0.5% CMC.

Comparison of the mass rates of the evaporation of benzene from a free surface and an insulated FHF layer ($\text{Na}_2\text{O}\cdot 2.5\text{SiO}_2(9\%)+\text{NaHCO}_3(9\%)+6\%\text{FA}+0.5\%\text{CMC}$) 5 cm high showed that the foam slows down the evaporation benzene 9 times. For FHF without the addition of CMC, the slowdown in evaporation was 5 times. Studies were also carried out for FHF ($\text{Na}_2\text{O}\cdot 2.5\text{SiO}_2(9\%)+\text{NaHCO}_3(9\%)+6\%\text{FA}+0.5\%\text{CMC}$) 5 cm high after 5 days of exposure indoors at $(20 \pm 2)^\circ\text{C}$ With and for FHF of the same composition, but without the addition of CMC ($\text{Na}_2\text{O}\cdot 2.5\text{SiO}_2(9\%)+\text{NaHCO}_3(9\%)+6\%\text{FA}$). The corresponding results are shown in Fig. 6.

The results of measurements allow us to state that the addition of CMC significantly increases the insulating properties of FHF. Thus, with the addition of 0.5% CMC to the foam-forming system, the intensity of benzene evaporation with a 5 cm FHF layer thickness decreased by 9 times compared with evaporation from the free surface and 2 times less than evaporation through the FHF layer without CMC.

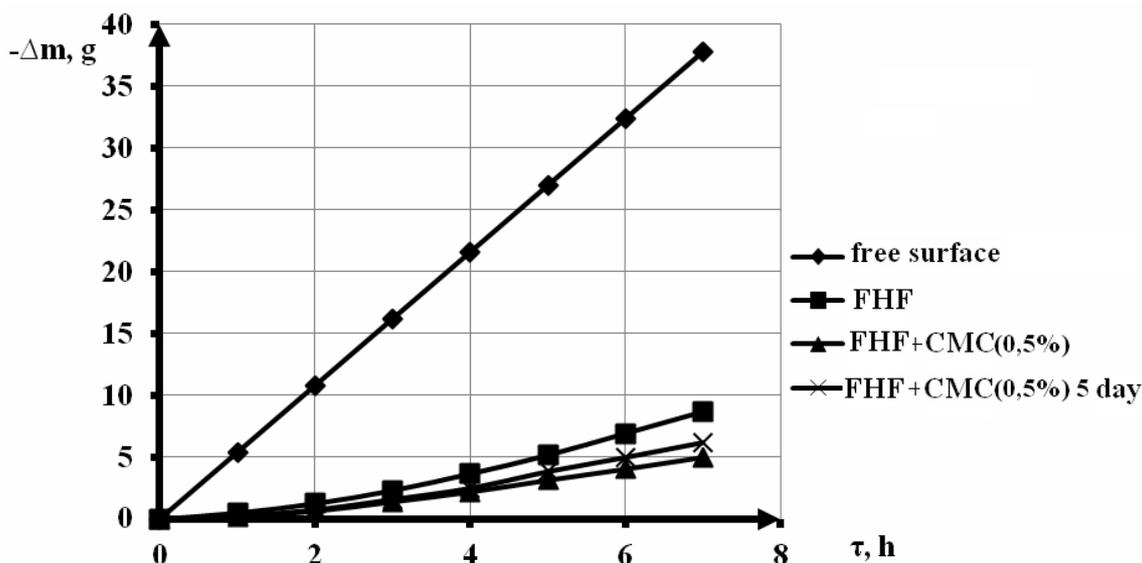


Fig. 6. The dependence of the benzene mass loss (Δm) due to evaporation from time (τ) from the free surface and through the FHF layer with a 5 cm foam layer thickness

Conclusions

It is shown that the main method of liquidation of emergencies caused by the spill of toxic liquids is the use of insulating layers of air-mechanical foams. However, they have significant drawbacks, the main of which are low resistance and insulating properties. To isolate the surface of toxic liquids, it is proposed to use a light material based on fast-hardening highly resistant foams. Obtaining fast-hardening highly resistant foams ensured the combination of the processes of gel and foaming. A liquid glass solution was used as a gelling agent. To increase the durability of fast-hardening foams, it was proposed to introduce into their composition non-volatile hygroscopic liquids (glycerin, ethylene glycol) or water-soluble polymers (carboxymethyl cellulose, polyvinyl alcohol). The best characteristics were shown by the fast-hardening foam of the composition $\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2(9\%) + \text{NaHCO}_3(9\%) + 6\%\text{FA} + 0.5\%\text{CMC}$. With a foam layer thickness of 5 cm, the mass evaporation rate of benzene decreases by more than 9 times compared to evaporation from the free surface. This foam retains its insulating properties for more than 5 days. The proposed insulating agent is close in insulating property to the previously proposed insulating materials based on silicates [11–13], however, it has an advantage over them in greater ease of application to the liquid layer. It is concluded that it is advisable to use fast-hardening highly resistant foams for the elimination of emergencies with the spill of toxic liquids.

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