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LIFETIME RESEARCH OF RAPID-HARDENING FOAMS

The results of the study of the time of existence of fast curing pins obtained on the basis of six gel-forming systems are presented. The time of destruction of fast curing pins was experimentally determined. It was found that the foam obtained on the basis of $\text{Na}_2\text{O} \cdot n\text{SiO}_2 + \text{NH}_4\text{Cl}$ system, which in the previous studies showed the best results in economic parameters, has the worst indicators of life time among the studied foams. The foam obtained on the basis of the $\text{Na}_2\text{O} \cdot n\text{SiO}_2$ (9 %) + NaHCO_3 (9 %) system was found to provide the greatest lifetime. It was established that the lifetime of the foam obtained on the basis of $\text{Na}_2\text{O} \cdot n\text{SiO}_2$ (9 %) + NaHCO_3 (9 %), at the height of the initial foam layer $h_{st} = 5$ cm, is 24 ± 2 h, and at $h_{st} = 10$ cm or $h_{st} = 15$ cm foam life is 48 ± 2 h. This figure is much higher than the lifetime of a similar layer of air-mechanical foam. The effect of the addition of foaming agent on the gel formation time is investigated. It was found that adding 2-6% foaming agent to the gel-forming systems does not change the gel-forming time for each of them. The effect of different types of foaming agents on the existence of fast curing foams has been investigated. It has been experimentally found that a 6 % «Morskoy» foaming agent provides the highest stability of fast curing foam over time. The foam obtained with the addition of "SOFIR AFFF 6%" (fluoro-synthetic film-forming) foam has the worst performance. All other foaming agents gave a positive result close to that of the «Morskoy» foaming agent. It is proposed to increase the time of loss of fluidity for the investigated gel-forming systems to 150 s. It was found that with increasing initial thickness of the fast curing foam layer, its lifetime increases.

Keywords: fast-hardening foam, gel formation, foam lifetime, foaming agent, gel-forming system, gel-forming agent, gel-forming catalyst

1. Introduction

Thousands of accidents occur annually throughout the world in the production, storage and transportation of hazardous chemicals (HC), the largest of which take on massive consequences. Therefore, their prevention and elimination remains an urgent problem.

The emergency response process is fully dependent on the facility (location), the nature and development of chemical accidents. Therefore, a universal description of this process does not exist.

The main consequences of chemical accidents include:

- emissions (spills) of toxic and other gases or liquids;
- instant or gradual evaporation;
- evaporation of gases with neutral and positive buoyancy;
- evaporation of heavy gas, ignition of liquids, buildings, structures, etc. explosions of a different nature (limited, in free space, explosions of vapor clouds, dust explosions, detonations, physical explosions, explosions of a condensed phase)

The main consequences of accidents:

- destruction of buildings, equipment, production lines, etc.;
- ignition of buildings, structures, liquids, etc. environmental contamination (atmospheric air, soil, water, technological equipment, etc.);
- defeat of people who find themselves in the zone of toxic effects without the necessary protective equipment or did not have time to use them.

In general, accidents with acute respiratory infections can be divided into four types:

- with the formation of only the primary HC cloud;
- with the formation of the strait, the primary and secondary HC;
- with the formation of the strait and only the secondary HC cloud;
- with environment contamination (soil, water sources, technological equipment, etc.).

The main means of localizing emergency situations associated with the spill of toxic liquids is air-mechanical foam. But foam has a significant drawback – a short lifetime. Most foam breaks down significantly in less than one hour. In the case of attempts to isolate polar toxic liquids, the foams are destroyed in a time not exceeding several minutes. To eliminate this drawback, it is proposed to use rapid-hardening foams (RHF). Such foams can exist from several hours to several years. To select a specific foaming system that will ensure the formation of solid foam with a long lifetime, it is necessary to conduct a series of studies of factors affecting their lifetime. The development of such foam will solve the problem of the short lifetime of existing foams that are used to isolate spills of toxic liquids.

2. Literature review and problem statement

Analysis of HC accidental spills with their subsequent evaporation indicates that they are of great danger due to contamination of soils, surface and ground waters, the death of flora and fauna [1]. At the initial stage of such accidents the greatest danger is the spread of a pair of toxic substances.

There are many ways to slow the evaporation from the surface of a spilled HC [2]. A common disadvantage is the insufficient lifetime of the insulation. To increase the lifetime of the insulation means, it is proposed to use means with an increased duration of action [3]. So, for example, in [4] it was proposed to use ultralight surface-active composite systems to minimize the evaporation of low boiling hydrocarbons and flammable liquids. This can be effective for isolating the substance that is in the tank, but in the event of an accident with the HC spill over a large area of use of such composites it becomes inappropriate. The disadvantage of such tools is their high cost and the difficulty of applying them to large surfaces.

Recently, a large number of works have been aimed at studying the insulating properties of foams [5], and rapid-hardening foams (RHF) [6]. In the work [7], the authors investigate RHF as an insulating agent against HC evaporation. For 15 HCs of various toxicities, in the laboratory, the process of evaporation through the RHF layer was studied. The disadvantage of such insulating agents is the presence of toxic components in their composition.

Also in the literature there are often examples of the RHF use as a fire extinguishing agent [8].

In a previous work [9], a method was developed for preparing rapid-hardening foams using sodium polysilicates with a silicate module of 2.5 ($\text{Na}_2\text{O} \cdot 2,5\text{SiO}_2$) as a gel-forming agent. Potassium dihydrogen phosphate (KH_2PO_4) and sodium hydrogen carbonate (NaHCO_3 – baking soda) were used as gelation catalysts. It was justified the possibility of using foam to isolate the surface of toxic liquid with hardening time; To obtain such foams, it was proposed to combine the processes of gelation (yield loss) and foaming.

In [10], the dependence of the gelation rate (τ , s) on the concentration of the gelation catalyst (NH_4Cl) and $(\text{NH}_4)_2\text{SO}_4$) was studied for various concentrations of the gel former (LG) – liquid glass ($\text{Na}_2\text{O} \cdot 2,5\text{SiO}_2$). It is concluded that, according to economic

and environmental parameters, it is advisable to use the $\text{Na}_2\text{O} \cdot 2.5\text{SiO}_2$ (3%)+ NH_4Cl (5%) system to obtain insulating foams.

An important characteristic of insulating agents is their stability. Therefore, for a full RHF study, it is necessary to establish their lifetime.

3. The aim and objectives of research

The aim of the experimental studies is to establish the gel-forming system (GFS)-based RHF lifetime and the influence of various factors on the RHF lifetime. To do this, it is necessary to solve the following objectives:

1. Experimentally determine the effect of the GFS composition on the foam lifetime.
2. Determine the effect of the type and concentration of the foaming agent on the GFS-based RHF lifetime.

4. Materials and methods for the study of gel-forming systems

Based on the results of previous studies [9, 10], 6 GFSs are selected for a detailed study of the RHF lifetime (Tab. 1)

Tab. 1. The studied concentrations of the components of the gel-forming systems (ω_1) and (ω_2)

№	First component	Second component	The main reaction product	ω_1 , %	ω_2 , %
1	$\text{Na}_2\text{O} \cdot n\text{SiO}_2$	NaHCO_3	H_2SiO_3	9	9
2	$\text{Na}_2\text{O} \cdot n\text{SiO}_2$	$\text{NH}_4\text{H}_2\text{PO}_4$	H_2SiO_3	6	7,5
3	$\text{Na}_2\text{O} \cdot n\text{SiO}_2$	NH_4Cl	H_2SiO_3	6	5
4	$\text{Na}_2\text{O} \cdot n\text{SiO}_2$	NaH_2PO_4	H_2SiO_3	6	5
5	$\text{Na}_2\text{O} \cdot n\text{SiO}_2$	$(\text{NH}_4)_2\text{SO}_4$	H_2SiO_3	6	5,5
6	$\text{Na}_2\text{O} \cdot n\text{SiO}_2$	$(\text{NH}_4)_2\text{CO}_3$	H_2SiO_3	6	16

Previously, it was found that it is necessary to increase the time interval for the RHF formation from 30-60 s to 30-150 s, since gelation in systems 1, 4, 5 occurred after 120 s, and in system 4 gelation occurred in a very narrow range of gel-forming concentrations (5-5.5)%.

Previous studies have found that for most systems, the accepted gel-forming agent concentration is 6%. This is due to the fact that when using lower concentrations of sodium silicate, the gel time was more than 180 s, and when using higher concentrations, gel formation was very fast (5-20) s, which does not meet the specified criteria. The exception was system 1, where the gelation process did not occur until a gel-forming concentration of 9% was reached.

Working solutions of gelation catalysts were prepared by the volumetric method from saturated solutions (concentrates) using the formula:

$$\omega_1 = \frac{V_1 \cdot \rho_1 \cdot \omega_1^0}{V_1 \cdot \rho_1 + V_2 \cdot \rho_2}, \quad (1)$$

where ω_1 – mass content of the substance in the concentrate; V_1 , V_2 – volume of concentrate and water; ρ_1 , ρ_2 – density of the concentrate and water.

Working solutions of the gelling agent were prepared by the volumetric method of liquid glass with concentrations of 36 wt. %. The density of the solutions was determined by the aerometric method.

GFS-based RHF lifetime was determined as follows. First, the working gel-forming solutions and 6 different gel-forming catalysts with the addition of a foaming agent were prepared. Then, the same volumes of working solutions (20 ml each) of the

gelation catalyst and gel-forming agent with the addition of a foaming agent of various concentrations (2, 4, 6%) were poured into a container with a wide mouth with a volume of 1 l and shaken them for 10-15 s. After mixing the components, the contents of the container were poured onto a flat horizontal surface and the initial height of the formed RHF was recorded and the behavior of the system and the control measurements of the height and integrity of the foam layer were monitored. The initial foam heights were 5, 10 and 15 cm. During the working day (8 hours), the height of the foam and the integrity of its surface layer were measured every hour. The studies were carried out at ambient temperature (18 ± 2) °C.

5. The results of an experimental study of the rapid-hardening foam lifetime based on gel-forming systems

For each GFS, the experiment was carried out three times, from the obtained results the arithmetic mean values of the height of the foam layer were calculated. The obtained results on the RHF stability are presented in Fig. 1, 2. The reproducibility of the results was ± 0.5 cm.

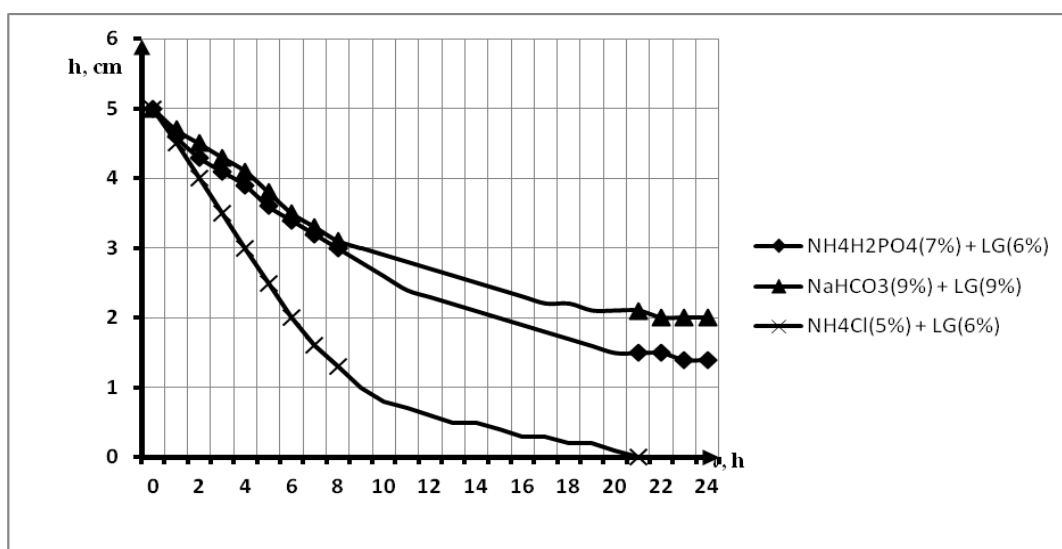


Fig. 1. A graphical representation of the change in the RHF layer thickness (h, cm) in time (τ , h) for systems 1, 2 and 3

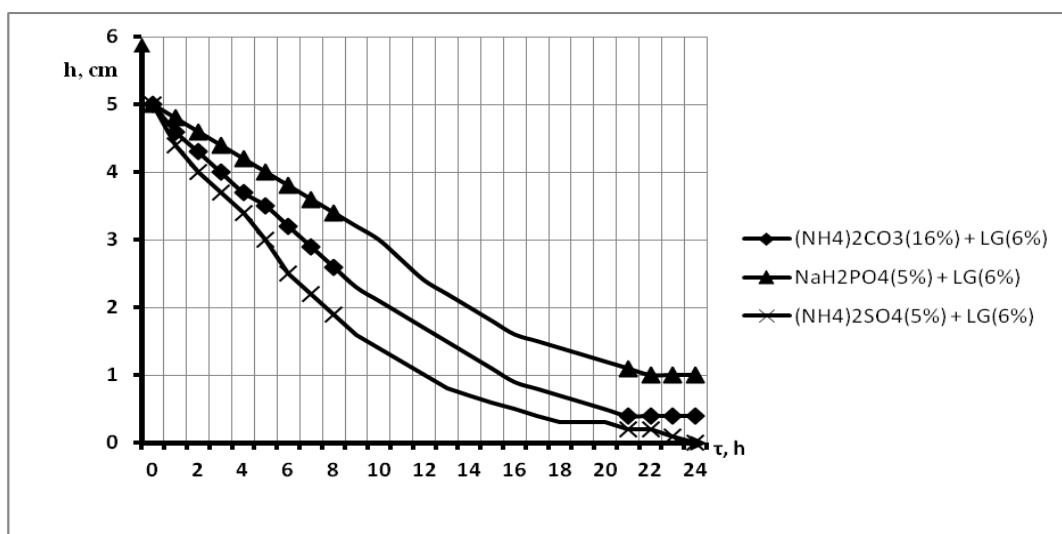


Fig. 2. A graphical representation of the change in the RHF layer thickness (h, cm) in time (τ , h) for systems 4, 5 and 6

After studying the RHF lifetime, it was found that out of the six studied GFSs, system 1 was stable. This allowed to conduct more detailed experiments with the selected system (NaHCO_3).

By the method described above, foam was obtained with a height of 5, 10, and 15 cm, and was observed for 48 hours. The observation results are presented in Fig. 3.

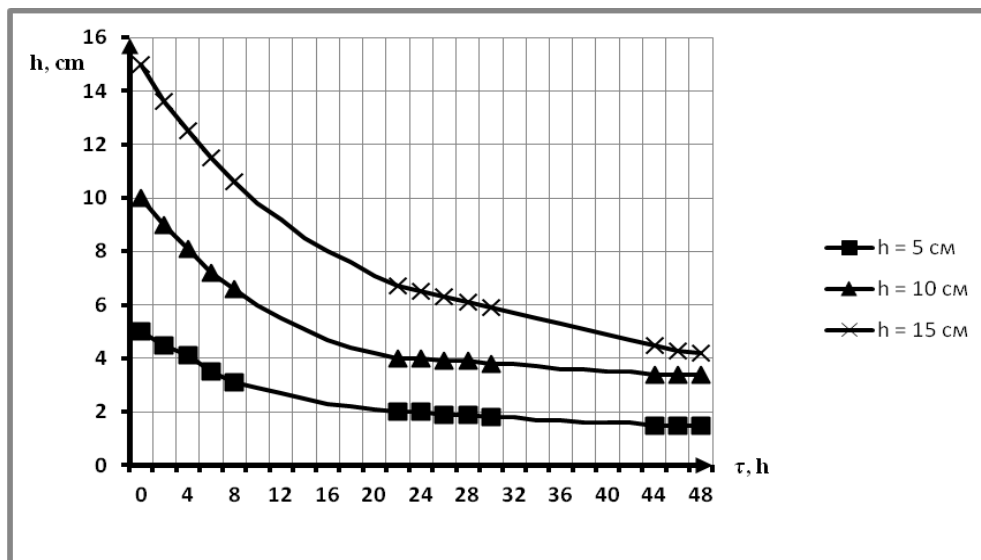


Fig. 3. A graphical representation of the change in the RHF layer thickness (h , cm) in time (τ , h) for system 1

Observation of the RHF behavior allows to state that over time water gradually evaporates from the foam, the content of which in the foam is ~90%, which leads to drying and gradual sprinkling of the upper layer of foam. After 0.5–1 day, depending on the initial height of the foam layer and the GFS type, the foam loses half of its volume. After 1–2 days of drying, RHF leads to the formation of cracks penetrating the entire residual layer of foam.

6. Results of an experimental study of the influence of the type and concentration of the foaming agent on the lifetime of the rapid-hardening foams

The next step was the study of the influence of the type and concentration of the foaming agent on the RHF lifetime and the gelation time of selected systems. For this let's use (synthetic and fluorosynthetic) foaming agents "Morskyi", "SOFIR AFFF 6%", "Teol", "Alpen".

The results show that when foaming agents were added, gelation occurred within acceptable limits for all GFS. The determination of the effect of the type of foaming agent on the RHF lifetime was carried out according to the following algorithm: the foaming agent was added to the GFS in concentrations of 6% of the total volume of the GFS and the obtained RHF was worked out by the developed method. The "Morskyi" foaming agent, which is used to extinguish fires at facilities in the area where they are located, is deficient in fresh water and in areas with a high content of calcium and magnesium salts in water. "SOFIR AFFF 6%" (fluorosynthetic film-forming) turned out to be the worst foaming agent, since this foaming agent is designed to produce foam of low multiplicity, which in turn led to the formation of a thin initial layer of foam. All other foaming agents also gave a positive result close to the result of the "Morskyi" foaming agent.

7. Discussion of the research results of gel-forming systems

The studies show that of the six selected GFS, the best results are shown by 2 systems $\text{Na}_2\text{O} \cdot n\text{SiO}_2 + \text{NaHCO}_3$ and $\text{Na}_2\text{O} \cdot n\text{SiO}_2 + \text{NH}_4\text{H}_2\text{PO}_4$. $\text{Na}_2\text{O} \cdot n\text{SiO}_2 + \text{NaH}_2\text{PO}_4$ system also shows a result close to system 1, but is eliminated, since the gelation in this system occurred in a very narrow range of gelation catalyst concentrations (5 - 5.5%), which can cause additional complications in obtaining . $\text{Na}_2\text{O} \cdot n\text{SiO}_2 + \text{NH}_4\text{Cl}$ system, although it proved to be the most promising of all the systems studied in previous works, shows the worst result when studying its lifetime. Visual observation of this system indicates that after 6 hours the top layer of foam dries and is covered with deep cracks, however, it can be observed that due to 9 hours it completely loses its integrity, as indicated by cracks through the entire layer of foam and loss of more than 80% of the initial volume of foam. The other two systems $\text{Na}_2\text{O} \cdot n\text{SiO}_2 + (\text{NH}_4)_2\text{CO}_3$ and $\text{Na}_2\text{O} \cdot n\text{SiO}_2 + (\text{NH}_4)_2\text{SO}_4$ show average results, which does not exclude the possibility of their further more detailed study.

Systems 1 and 2 decompose more slowly and maintain the integrity of the surface foam layer for more than 8 hours at an initial layer thickness of RHF of 5 cm. This result is an order of magnitude longer than the lifetime of a similar layer of air-mechanical foam.

The studied $\text{H}_2\text{O} \cdot n\text{SiO}_2 + \text{NaHCO}_3$ system showed the best results. Studies have also shown that a further increase in the foam layer to 15 cm at first leads to a rapid RHF subsidence (15 cm), and after 2 days, the height of the RHF layer (15 cm) does not differ from the RHF height (10 cm).

Thus, out of the six investigated GFSs, for the purpose of obtaining quick hardening foams, it is proposed to use the $\text{Na}_2\text{O} \cdot 2,5\text{SiO}_2$ (9 %) + NaHCO_3 (9 %) system, the lifetime of which can be controlled by changing the thickness of the initial foam layer, the maximum lifetime of which is 48 ± 2 hours.

8. Conclusions

1. It is found that the lifetime of a foam based on the $\text{Na}_2\text{O} \cdot n\text{SiO}_2$ (9 %) + NaHCO_3 (9 %) system is the longest, it is 24 ± 2 for an initial thickness of 5 cm, and 48 ± 2 hours for an initial thickness of 15 cm, which in turn is an order of magnitude longer than the lifetime of a similar layer of air-mechanical foam. The experiments showed that the $\text{Na}_2\text{O} \cdot 2,5\text{SiO}_2$ (3 %) + NH_4Cl (5 %) GFS, which was studied in previous works and had better results, has the worst foam stability result. After 5 – 6 hours, the foam loses half of its original thickness, and after 14 - 16 hours it completely collapses, while other samples have minor damage. With an increase in the initial thickness of the RHF layer, its lifetime increases.

2. “Morskyi” foaming agent with a concentration of 6% provides a maximum lifetime of PCT. The worst foaming agent was “SOFIR AFFF” 6% (fluorosynthetic film-forming). Studies have shown that a change in the concentration of the foaming agent in the range from 2% to 6% does not affect the stability of the foam, and does not affect the gelation time. Adding concentrations of a foaming agent of less than 2% leads to the formation of unstable foam of low multiplicity. An increase in the concentration of the foaming agent in the system of more than 6% becomes impractical. Other foaming agents gave a positive result close to the result of the “Morskyi” foaming agent.

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ДОСЛІДЖЕННЯ ЧАСУ ІСНУВАННЯ ПІН ШВИДКОГО ТВЕРДНЕННЯ

Представлені результати дослідження часу існування пін швидкого тверднення отриманих на основі гелеутворюючих систем. Експериментально визначено час руйнування пін швидкого тверднення. Встановлено, що піна, отримана на основі системи $\text{Na}_2\text{O} \cdot n\text{SiO}_2 + \text{NH}_4\text{Cl}$, яка в попередніх дослідженнях показала найкращі результати за економічними параметрами, має найгірші показники часу існування серед досліджуваних пін швидкого тверднення. Встановлено, що найбільший час існування у піни на основі системи $\text{Na}_2\text{O} \cdot n\text{SiO}_2$ (9 %) + NaHCO_3 (9 %). Встановлено, що час існування піни, отриманої на основі системи $\text{Na}_2\text{O} \cdot n\text{SiO}_2$ (9 %) + NaHCO_3 (9 %), при висоті початкового шару піни $h_{\text{поч}} = 5$ см, складає 24 ± 2 год, а при $h_{\text{поч}} = 10$ см та $h_{\text{поч}} = 15$ см час існування піни складає 48 ± 2 год. Цей показник на порядок перевищує час існування аналогічного шару повітряно-механічної піни. Експериментально встановлено, що додавання 2–6 % піноут-

ворювача до гелеутворюючих систем не змінює час гелеутворення. Досліджено вплив різного типу піноутворювачів на час існування пін швидкого тверднення. Експериментально встановлено, що піноутворювач «Морський» з концентрацією 6 % забезпечує найбільший час існування піни швидкого тверднення. Піна, отримана з додаванням піноутворювача «SOFIR AFFF 6 %» (фторсинтетичний плівкоутворюючий), має найгірші показники часу існування. Інші досліджувані піноутворювачі дали позитивний результат близький до результату піноутворювача «Морський». Запропоновано збільшити час втрати текучості для досліджуваних гелеутворюючих систем з 30–60 с до 150 с. Встановлено, що зі зростанням початкової товщини шару піни швидкого тверднення збільшується час її існування.

Ключові слова: піна швидкого тверднення, гелеутворення, час існування піни, піноутворювач, гелеутворююча система, гелеутворювач, каталізатор гелеутворення

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