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International Scientific Conference «Social and Cultural Transformations in the Context of
Modern Globalism»ADDRESSING THE ENVIRONMENTAL CHALLENGES AND
FIRE SAFETY BY MEANS OF MATERIALS ENGINEERING

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Abstract

The article describes the results of studies aimed to assess the effect of zeolites with microencapsulated water on the fire-retardant efficiency of fire-retardant intumescent compositions using epoxy resins under the influence of hydrocarbon flaring. As part of a comprehensive research initiative, scientists conducted a series of experiments to evaluate the effect of microencapsulated zeolites on the fire retardant performance of fire-retardant intumescent epoxy resin compositions. These compositions were exposed to prolonged hydrocarbon flaring to simulate severe fire conditions. An advanced static method, regression analysis, was used to quantify the effectiveness of fire retardants. This approach allowed scientists to establish correlations between key parameters and fire resistance of the studied compositions. The research also included the development of an innovative technology for the synthesis of fire-retardant coatings that combine ablative and desorption protection mechanisms. These coatings have demonstrated exceptional fire-retardant properties, providing effective protection against thermal stress. Analysis of regression models revealed several critical factors. Thermal effect of exothermic peak (at 600-700°C): Microencapsulated zeolites have the ability to release water upon exothermic decomposition, which leads to cooling of the composition and additional foaming. These findings have important implications for the design and optimization of flame retardant materials, providing greater understanding of the mechanisms underlying their effectiveness.

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Keywords: Combustion of hydrocarbons, coefficient, exothermic peak, hydrocarbon fires, regression analysis, swelling thermal effect



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1. Introduction

Fire danger at oil and gas industry facilities (OGI) is directly related to the volume and characteristics of the flammable load present in them. Hydrocarbon fires that occur at oil and gas fields contribute to a significant increase in temperature, which has a significant impact on load-bearing structural elements. In order to prevent their destruction, they are treated with fire retardant intumescent compounds (FRIC), which, when exposed to elevated temperatures, form a protective thermal insulation layer. The effectiveness of such coatings directly depends on their performance characteristics (Dokuchayeva et al., 2024; Tang & Yang, 2024). However, existing fire retardant compounds used at oil and gas industry facilities demonstrate insufficient effectiveness in conditions of hydrocarbon combustion in flare mode. This circumstance necessitates the development of more reliable and effective fireproof solutions to ensure fire safety at oil and gas fields (Tsoi, 2016).

The main disadvantage of these methods is the possibility of their application only in production conditions, high toxicity of combustion products, changes in the chemical composition with a deterioration in the operational properties with a high content of the modifier in the FRIC.

One of the existing ways to improve the operational characteristics of the FRIC is the deposition of functional components in the FRIC formulation. Porous fillers with microencapsulated fire-extinguishing agents (FEA) can increase the fire-retardant characteristics of FRICs.

2. Problem Statement

The object of the study was the fire retardant composition "TERMOBARIER" 2. Natural zeolites 40 µm in size were used as modifying elements with microencapsulated water adsorbed by active diffusion (Lipich & Balahura, 2024; Regnerová et al., 2024; Shumilina & Antsiferova, 2024).

The components were obtained by mixing a modified hardener and a thermoplastic film former. Microencapsulated zeolites were introduced into the hardener at a concentration of 1–5% of the mass. After mixing the hardener with the film former, the resulting mixture was stirred mechanically to a homogeneous state (Ahmad et al., 2024; Singh et al., 2024; Waite, 2024).

The fire retardant composition was applied on the basis of technological regulations for the main composition. St3 steel plates with dimensions of 100x50x6 mm were used as a substrate.

The study of the fire retardant efficiency of the products was carried out on a laboratory machine simulating the temperature and erosive effects of the hydrocarbon flame (Tsoi, 2016). The products were placed in a test chamber, the temperature of the back side of the plate was measured by two thermocouples, the propane-butane burner had a mass flow rate of combustible gas of 50 ... 60 g/h and a pressure of 0.1 MPa, the temperature of the gas flow was measured by thermocouples (Tsoi, 2016). The limiting state was taken to reach the back side of the plate of 500°C in accordance with GOST R 53295-2009.

The thickness of the fire retardant layer was measured with an MT-201-00 magnetic thickness gauge (GOST R 51694, ISO 2808). The thickness of the swollen layer was determined with a caliper (Lyz, 2014).

To determine the degree of influence of fillers on the operational characteristics and fire-retardant efficiency of the HVAC, it seems necessary to construct a mathematical model of the system under study.

In order to solve the regression problem, the time of the onset of the limiting state of the protected surface with FRIC was simulated (Medova, 2020); the modeling tool was the REGRAN computer program (Tarantsev et al., 2016). To assess the influence of input factors (IF) – $X_1 \div X_7$ (Table 1) on the output parameter (OP), the onset of the limiting state (Y) with various combinations of OF was determined (Figure 01). To obtain a reliable estimate, the experiments were carried out five times.

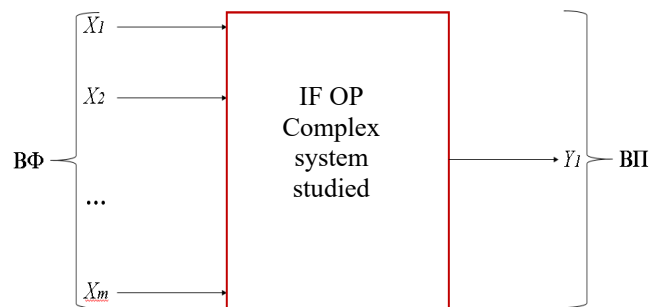


Figure 1. System model The OP will be determined using equation (1) (Tarantsev et al., 2016) $y = f(X_1, \dots, X_7)$ (1)

3. Research Questions

A number of experimental studies have been carried out to confirm the possibility of using zeolites with microencapsulated water as a modifying agent for FRIC, which improved the operational characteristics of the fire retardants (Ivakhnyuk et al., 2019). However, the deposition of most types of FEA in the FRIC is limited due to the incompatibility of these components with some types of polymer bases (Ivakhnyuk & Stolyarov, 2018). The method of active diffusion allows you to store and deposit substances of various classes in adsorbents without loss of sorbent until the external conditions of the environment (temperature, pressure, chemical action) change, which makes this method promising for increasing the operational characteristics of FRICs used under high temperatures (Keltsev, 1984).

4. Purpose of the Study

In [2], thermal and adhesive properties of the FRIC modified with microencapsulated zeolites were evaluated. It was found that the addition of zeolites with microencapsulated water (3% wt.) improves the operational characteristics of the FRIC:

- i. improves the adhesion strength of FRIC to the protected surface;
- ii. increases the total thermal effect during the thermal decomposition,
- iii. increases the coke residue;
- iv. reduces the flammability of the material;
- v. reduces the rate of weight loss of a substance.

To assess changes in fire retardant efficiency for various combinations of factors ($X_1 \div X_7$), a regression analysis can be carried out.

5. Research Methods

Table 1. Composition of variables for a regression analysis

Designation	Feature	Measurement unit
X_1	Concentration of zeolites in the hardener, φ	%.
X_2	Adhesion strength	kgf / cm ²
X_3	Swelling coefficient (K_{sw})	h_{bc}/h_0
X_4	Flammability KI	%
X_5	specific heat of exothermic reactions in the temperature range	J / g
X_6	Heat of exothermic peak 2	J / g
X_7	Heat of exothermic peak 3	J / g
Y	Time to reach the limiting state of the protected surface..	min

The regression analysis of the limiting state of the protected surface with the FRIC under the thermal and erosive effects of flaring (Nikolaeva, 2014) combustion of hydrocarbons involved:

1) Building a quasi-linear regression equation (Tarantsev et al., 2016) of the dependence of the limiting state of the protected surface with the FRIC on the performance characteristics of the fire retardant.

2) Selection of conditional factors by the forced search method.

3) Calculation of the regression coefficient by the least squares method.

4) Evaluation of the adequacy of the regression analysis results by the Fisher's test and calculating the criterion for the maximum mismatch between the experimental and calculated IP values.

Using the REGRAN program, regression coefficients were calculated and conditional factors were selected. The dependence of the IP on the OF is described by a set of adequate equations; therefore, the multi-model principle was used to construct the regression models, which ensures the objectivity of the forecast of the output parameter (Y_1) and the result of assessing the significance of the input factors ($X_1 \div X_7$).

The dependence of the fire retardant efficiency on the operational FRIC characteristics is expressed by the quasilinear regression equation (Tarantsev et al., 2016).

$$y = \sum_{i=1}^M b_i h_i, (2)$$

where b_i – i-th regression coefficient; b_i – i-th calculated regression coefficient; h_i – i-th conditional factor, determined depending on the IF $X_1 \div X_7$; K – number of regression coefficients or conditional factors ($K < N$).

Values $\{h_i\}$ were determined by the search method, $\{b_i\}$ – using the least squares method under condition (3):

$$D_j = (N - K_j)^{-1} \cdot \sum_{j=1}^N (a_{ji}^E - a_{ji}^V)^2 \rightarrow \min, (3)$$

where a_{ji}^E, y_{ji}^V – obtained by regression equation (2) during the i-th test, the values of the j-th OP, respectively, for the i-th combination of IF.

Adequacy of equation (2) [8] was assessed by the Fisher's criterion F [9], with an accuracy sufficient for engineering calculations (expression 4) and maximum mismatch Δ between the experimental and calculated values of OP (expression 5):

$$F_j = \frac{D_{jo}}{D_j}, (4)$$

where D_{jo} – dispersion of experiences.

$$\Delta = \max_{i=1}^N |a_{ji}^3 - a_{ji}^B|. (5)$$

Using the REGRAN program, the regression coefficients $\{b_i\}$ were calculated and the conditional factors (h_1, \dots, h_k) were selected. The dependence of the IP on the OF is described by a set of adequate equations; therefore, the multi-model principle was used to construct the regression models [10], which ensures the objectivity of the forecast of the output parameter (Y_l) and the result of assessing the significance of the input factors ($X_l \div X_7$).

6. Findings

The experiments showed that the addition of zeolites to the FRIC improves the characteristics under study (Figure 02). When exposed to flaring combustion of hydrocarbons, the control sample reaches the limiting temperature of 500°C at 65 minutes, while the samples modified with microencapsulated zeolites are able to withstand this test mode more efficiently by 80% for samples with a concentration of zeolites in the hardener of 1–5 % mass.

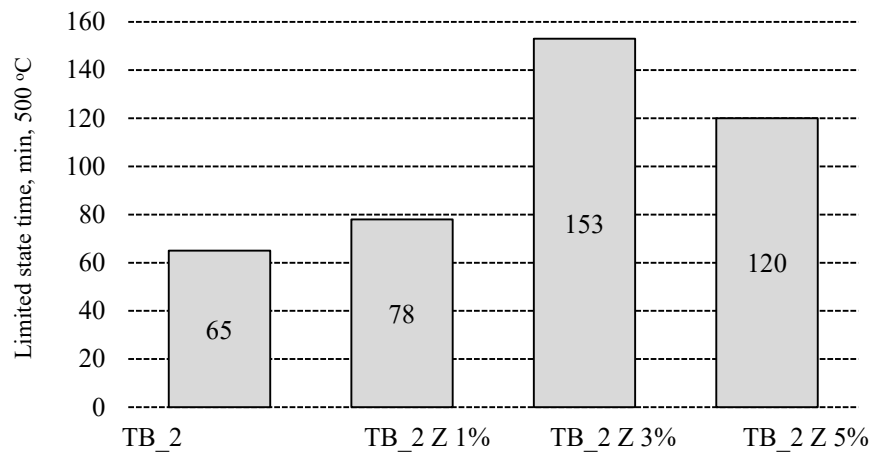


Figure 2. Histogram of indicators of the fire-retardant efficiency of test samples in the conditions of flare combustion of hydrocarbons. (TB_2 – Thermal barrier 2; TB_2 C 1% Thermal barrier 2 containing zeolites with 1% microencapsulated water)

Using the results of firing tests, the swelling coefficient (K_{sw}) was determined by formula

$$K_{sw} = h_{sw}/h_0 (5)$$

where h_{sw} – expanded layer thickness, h_0 – initial layer thickness.

The study found that addition of zeolites helps to reduce the swelling coefficient by 12.7% (Table 02).

Table 2. Values of the swelling coefficient as a result of concentration of zeolites

	Concentration of zeolites in HVAC, wt. %					
	0	1	2	3	4	5
K _{sw}	2,00	1,70	1,75	1,82	1,80	1,74

The results of the regression analysis of the limiting state of the samples are presented in Table 03.

Table 3. Regression models

Regression equations (6)	F	Δ
$Y_1 = 17,29 \cdot X_1 \cdot X_3^2 - 2,416 \cdot X_1^2 \cdot X_3^2 - 38,03X_3 + 34,93X_3^2$	21,0	6,96
$Y_1 = -8,814 - 11,09 \cdot X_6^2 + 11,84 \cdot X_3^2 \cdot X_6$	72,6	4,91
$Y_1 = 9,751 \cdot X_1^2 \cdot X_3 \cdot X_6^2 - 1,081 \cdot X_1^2 \cdot X_3 \cdot X_6 + 13,17 \cdot X_1 \cdot X_3^2 + 16,11 \cdot X_3^2$	777,0	1,32
$Y_1 = -842,7 \cdot X_1^2 \cdot X_6^2 - 11,27 \cdot X_2 \cdot X_6 + 47,77 \cdot X_3 \cdot X_6$	210,0	3,31

Based on the results of the regression analysis, the main influencing factors were identified (in the sequence of decreasing their influence on the OP):

- i. X1 (concentration of zeolites in the hardener)
- ii. X3 (swelling coefficient);
- iii. X6 (Q of exothermic peak 2).

The input factors X2, X4, X5 and X7 were not used due to the high cross-correlation.

The use of the mathematical apparatus makes it possible to develop recommendations for improving the operational characteristics of fire retardant coatings in conditions of flare combustion of hydrocarbons.

The results obtained made it possible to develop a methodology for increasing the fire-retardant efficiency of fire-retardant coatings, which is used in the technological audit of oil and gas companies.

The technique for improving the performance of fire retardant coatings includes the following stages:

- 1) Analysis of the technological state of the complex technological audit of the oil and gas company.
- 2) Determination of the compliance of the fire-retardant efficiency of the applied fire-retardant coatings with the operating conditions.
- 3) Determination of the possibility of synthesizing the modifying component with the FEA film former.
- 4) Analysis of the operational properties of FRIC (adhesive strength (W2), swelling coefficient (Ksw), heat of exothermic peak 1 (Qdsk1), heat of exothermic peak 2 (Qep2), heat of exothermic peak 3 (Qep3), oxygen index (OI));
- 5) Prediction of performance parameters (according to formulas (6):
 $Tps.=f(Yoz.ef.)$
- 6) Based on the prediction results for the parameters of operational characteristics of the modified FRIC, the following condition must be met

$$Yoz.ef.>Yoz.ef. BP$$

7) Preparation of a modifying additive in accordance with the characteristics of synthesis of fire retardant coatings.

8) Implementation of the technology for the synthesis of ablation-desorption fire-retardant coatings in order to ensure the required limit of fire resistance of metal structures of equipment for oil and gas facilities.

Integration of the principles of creating ablative-desorption fire-retardant coatings helps achieve the required level of fire resistance of metal structures. A key aspect of this technology is reagent-free modification and improvement of performance properties through the use of functional components in fire retardant coating (FRIC) formulations. The different types of fire retardants used in FRIC have unique characteristics that affect the overall fire retardant properties of the coating. These flame retardants can be classified according to their mechanism of action:

- i. Flame retardants: Delay or prevent the ignition of a substrate by forming a protective barrier or releasing non-flammable gases.
- ii. Flame retardants: Reduce the speed of flame propagation and release non-flammable gases, diluting flammable vapors.
- iii. Intumescent agents: Create an expanded carbon foam when exposed to heat, insulating the substrate and slowing heat transfer.
- iv. Endothermic Agents: Absorb heat during decomposition, cooling the environment and slowing the spread of fire.

The effectiveness of FRIC depends on the careful selection and combination of fire retardants, as well as their dispersion and adhesion to the metal surface. Reagent-free modification of FRIC formulations involves the use of functional components that improve the compatibility of components, increase coating adhesion and enhance fire retardant properties. Advanced FRICs with optimized compositions and functional components provide superior fire resistance to metal structures, extending their safe operation in the event of a fire. (Popper, 2012).

An innovative method for creating fire-retardant coatings through the synthesis of ablative-desorption materials is becoming increasingly important in improving fire safety in the oil and gas industry. These coatings, known as FRICs (fire retardant inhibitors of hydrocarbons), play a critical role in the overall fire protection system, helping to prevent and extinguish fires in facilities. FRIC synthesis uses specialized functional components that are optimized to protect metal structures from the extreme thermal and erosive effects encountered in emergency situations. These components work in tandem to create a barrier that absorbs the heat generated by hydrocarbon flaring and prevents it from being transferred to the metal (Rorty, 2017). As a result of FRIC synthesis, the time of the limiting state of metal structures increases. This time represents the critical interval during which structures must withstand exposure to fire without failure. Extending this time gives oil and gas facility operators additional time to take fire containment and suppression measures, thereby increasing the safety of personnel, equipment and the environment. In addition, FRIC coatings have the ability to desorb non-flammable gases in response to thermal stress. These gases create an additional protective layer that cools the metal surface and inhibits the spread of fire. This desorption process also helps reduce the generation

of smoke and toxic emissions, creating more favorable conditions for personnel evacuation and firefighting.

7. Conclusion

The deposition of microencapsulated zeolites in the FRIC improves the fire retardant efficiency by 80%.

The regression analysis revealed that the factors of increasing the fire retardant efficiency when depositing microencapsulated zeolites in the FEA are:

- i. swelling coefficient;
- ii. thermal effect of the exothermic peak in the temperature range of 600–700°C;

The mathematical apparatus of correlation-regression analysis used to study the fire-retardant efficiency of modified fire-retardant coatings makes it possible to develop recommendations on the use of a technology designed to improve the performance of fire-retardant coatings under the flare combustion of hydrocarbons.

Results from a comprehensive analysis of the performance characteristics of fire retardant coatings enhanced with zeolite modifications have revealed the significant potential of FRIC (Fire Resistant Insulating Coatings) synthesis technology in combating hydrocarbon fires in critical sectors of the oil and gas industry. FRIC's innovative technology is based on the integration of zeolites, a class of microporous minerals with outstanding adsorption properties, into fire retardant coatings. These modified coatings exhibit superior fire-retardant properties, effectively retarding flame propagation and suppressing smoke and gas emission. The study demonstrated that zeolite additives optimize the physicochemical properties of fire retardant coatings by creating a multi-layered protective barrier. The microporous structure of zeolites provides excellent adsorption of hydrocarbon vapors and gases, reducing flammability and delaying heat transfer. In addition, zeolites release bound water when heated, forming a protective vapor curtain that cools the surface and prevents the spread of fire. The successful application of FRIC technology in the oil and gas industry opens up new opportunities for preventing and mitigating hydrocarbon fires. These coatings can provide reliable protection to facilities and equipment, reducing risks to personnel, the environment and economic losses.

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