1. Introduction

Given the unique properties of reed, such as small volumetric weight, low thermal conductivity, high atmospheric and chemical resistance, the possibility to manufacture parts at a construction site, articles made of reed are widely used in construction. This is especially true of the countries in Western Europe (the Netherlands, Denmark), where reed is used to make roofs and build wall thermal insulation. At the same time, the unresolved issues related to fire protection of products from such materials limit possibilities of their application. Resonant fires at facilities hosting many people (holiday homes, restaurants, cafes, etc.) indicate the relevance of such fire protection.

It is known that reed refers to cellulose-containing materials, which are not capable to burn on their own; under the influence of temperature, only the products of its decomposition ignite [1]. Introducing fire retardants to the material reduces the amount of combustible volatile products, inhibits the gas-phase flame responses, and rules out the flameless burning of carbonized residue [2, 3].
Recently, such means have become widespread that are capable of forming an insulation layer at the surface of a construction structure, which greatly reduces the processes of heat transfer to the material [4].

Given the peculiarities of chemical construction and structure of reed, the fire protection of articles made from reed is accompanied with difficulties to apply impregnating flame-retardant agents. Using the new ones needs reliable techniques to study the properties of coating. This has predetermined our research in this field.

### 2. Literature review and problem statement

Fire protection of reed employs impregnating agents that cover a construction structure, which is characterized by the decomposition of fire retardants under the action of temperature with the absorption of heat and the release of non-combustible gases. Paper [5] report results from studying a fire-retardant coating performance under the influence of temperature. The authors described both the behavior of a swelling coating and the subsequent heat transfer. However, the issue that remains unaddressed is the establishment of temperature for the foam coke formation, which reduces the quality of the results obtained. In most cases, such compositions are modified by polymer complexes and flame retardants; however, the agents are related to the materials that are characterized by low adhesion and, at high temperature, release toxic combustion products [6].

Study [7] defines the most promising fire-retardant compositions for swelling coatings, which represent complex systems of organic and inorganic components; however, the issue that has remained unaddressed relates to the manifestation of the joint effect of the coating components at swelling. The materials described in work [8] are characterized by high intumescent capability; the authors, however, failed to show the mechanism of coke formation and temperature transitions of the coating into foam coke.

The kinetics of forming a layer of foam coke, which forms at swelling, has its own peculiarities, and depends on the properties of substances [9]. Therefore, there is a need to study the conditions to form a barrier for thermal conductivity and to establish the effective action of a coating resulting in the formation of a coke layer. However, the appropriate physical-chemical calculations to confirm this process were not given. Thus, according to authors of [10], this is due to the formation, at the decomposition of fillers in the composition of a coating, of the significant number of high-temperature compounds that are compacted under temperature and form a strong skeleton.

Paper [11] suggested a model that takes into consideration the shape of pores. However, a given model does not take into consideration how changing the shape of pores affects the heat transfer to a structure itself. In addition, many coatings have a series of drawbacks, such as applying separate components, losing functional properties at increasing the temperature of the environment [12]. This means that it was not determined how the process occurs under conditions of temperatures in the range of a flame-retardant coating decomposition.

To reduce water solubility and washout of retardants from impregnating solutions and coatings, the surface of a fire-retardant material is treated with water repellents [13]. In addition, a fire-retardant composition is prepared based on organic binders that do not dissolve in water [14]. All these requirements are typical for wood while not always expedient for reed and require the elaboration of new approaches [15].

Given the above, it was found that for a material such as reed there are no data on improving its fire resistance and, accordingly, establishing the effectiveness of fire protection for a particular product, namely reed, which has specific properties and scope of application.

Therefore, it is a promising task to establish the thermal resistance of roofing products for reed under a long effect of temperatures and the impact of a mixture of inorganic and organic substances that are part of the coating composition in order to ensure thermal resistance to flame. The issues specified above necessitate a research in this field.

### 3. The aim and objectives of the study

The aim of this work is to study the efficiency of fire protection of reed by roofing impregnating compositions, which form a layer of coke under a thermal effect.

To achieve the set aim, the following tasks have been solved:

- to establish patterns in the deceleration of ignition process and the propagation of flame by reed when treated with a composition based on inorganic substances and polymeric complexes when the retardants are washed out;
- to assess the fire resistance of an article made from reed during field tests of mats made from reed under the action of a gasoline flame.

### 4. Materials and methods of research

#### 4.1. Materials that were examined in the experiment

We established the efficiency of fire protection of a roof- ing solution using the samples of reed the average size of up to 10 mm in diameter, 310 mm in length, which were arranged into mats the size of 310×140 mm with a thickness of 10...12 mm, treated with a roofing impregnating solution in the amount of 40.2 g/m². Specifically, the modified roofing impregnating solution «Skela-i» (a mixture of urea, 28...30 %, phosphorus acids, 23...24 %, and starch, 20 %); to increase resistance against water, this mixture was added a PVA-dispersion in the amount of 20 %. The resulting mass was stirred, we then added water to 100 % and applied on a reed sample.

To study the counteraction of a construction structure made from reed against high temperature under a gasoline flame, we used model samples of structures made from reed with a mat thickness of 60 mm, the average size of 700×280 mm (Fig. 1):

a) untreated (sample No. 1);

b) fireproof samples – mats made from reed were treated with flame retardant coatings in the amount of 0.4 kg/m² of surface:

- the modified roofing impregnating Solution «Skela-i» (experimental sample No. 2);
- the modified roofing impregnating Solution «Skela-i» with the addition of a PVA-dispersion (experimental sample No. 3).

We used automotive gasoline A92 as fuel.
4. 2. Procedure for determining indicators of the properties of reed samples

Our study into experimental determining of parameters for reed ignition was based on the procedure implying putting a sample into a test chamber and exposing it to a radiation panel influence. After the sample ignited, the ignition time was measured, as well as the maximum temperature of combustion products and the time to reach it, the time it took for a flame front to travel the surface sections, and the length of the burnt part of a sample [2].

A working procedure guided the field tests on the counteraction from a heat-insulating mat made from reed to a high temperature. In this case, the structure made from reed and treated with fire protection agents was exposed to the action of a gasoline flame with the assigned parameters; we then registered the sample’s mass loss after testing.

The criterion for determining the effectiveness of fire protection is the absence of a material’s burning, flame propagation over the surface, as well as the corresponding value for mass loss by a sample, which should not exceed 10 %.

5. Experimental study of reed fire-retardant effectiveness and results

The use of fireproof reed implies its exterior utilization for buildings, which is why it is a relevant task to establish conditions for the composition washout from reed surface, provided the experiment measures the relative concentration of a flame retardant in the ambient environment, for example in water.

In this regard, to determine the flame retardant’s efficiency in water, we conducted an experimental study. A sample of fireproof reed was placed in distilled water for a certain period, then, in line with procedure [16], we determined the amount of a flame retardant (urea phosphate) in water (Table 1).

Results of the study on experimental determining of the fire retardant’s washout from fire-protected reed, conducted under laboratory conditions, are shown in Fig. 2.

We have acquired regression data on the amount of the washed-out flame retardant during testing of fireproof reed, which are described by dependences of the following type:

\[ v(t) = a_0 + a_1 t + a_2 t^2, \]  

where \( t \) is the time to wash out a sample, \( s \); \( a_0, a_1, a_2 \) – regression coefficients.

Experimental data were treated by a least square method. We minimized the variance:

\[ D = \left[ v(t_i) - T_i \right]^2, \]

where \( v(t_i) \) are the theoretical values for the quantity of a fire retardant in water, determined from formula (2); \( T_i \) are experimental values.

After minimizing \( D \), we calculate the standard deviation \( \sigma \) from formula:

\[ \sigma = \sqrt{\frac{D}{n - n_0}}, \]

where \( n \) is the number of measurements; \( n_0 \) is the number of unknown parameters.

Results from processing experimental data on the combustion of wood samples are given in Table 2.

### Table 1

<table>
<thead>
<tr>
<th>Washout interval, min.</th>
<th>5</th>
<th>10</th>
<th>30</th>
<th>60</th>
<th>120</th>
<th>240</th>
<th>360</th>
<th>600</th>
<th>1,200</th>
<th>1,440</th>
</tr>
</thead>
<tbody>
<tr>
<td>protected wood samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with the modified roofing impregnating solution «Skela-i»</td>
<td>0.34</td>
<td>0.53</td>
<td>0.9</td>
<td>1.2</td>
<td>1.5</td>
<td>2.2</td>
<td>2.7</td>
<td>3.35</td>
<td>4.55</td>
<td>4.87</td>
</tr>
<tr>
<td>same, with PVA-dispersion added, 5%</td>
<td>0.001</td>
<td>0.18</td>
<td>0.24</td>
<td>0.31</td>
<td>0.49</td>
<td>0.8</td>
<td>1.158</td>
<td>1.44</td>
<td>1.6</td>
<td>1.64</td>
</tr>
<tr>
<td>same, with PVA-dispersion added, 15%</td>
<td>0</td>
<td>0.01</td>
<td>0.08</td>
<td>0.12</td>
<td>0.23</td>
<td>0.34</td>
<td>0.435</td>
<td>0.67</td>
<td>0.98</td>
<td>1.12</td>
</tr>
<tr>
<td>same, with PVA-dispersion added, 25%</td>
<td>0</td>
<td>0</td>
<td>0.006</td>
<td>0.031</td>
<td>0.056</td>
<td>0.091</td>
<td>0.16</td>
<td>0.2</td>
<td>0.34</td>
<td>0.41</td>
</tr>
</tbody>
</table>
Results from processing experimental data on the combustion of reed samples

<table>
<thead>
<tr>
<th>Sample of fireproof reed</th>
<th>Parameter value</th>
<th>(a_0)</th>
<th>(a_1)</th>
<th>(a_2)</th>
<th>(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>modified roofing impregnating solution «Skela-i»</td>
<td>0.5598</td>
<td>0.0065</td>
<td>(-3\times10^{-6})</td>
<td>4.32</td>
<td></td>
</tr>
<tr>
<td>same, with PVA-dispersion added, 5%</td>
<td>0.1288</td>
<td>0.0030</td>
<td>(-1\times10^{-6})</td>
<td>3.22</td>
<td></td>
</tr>
<tr>
<td>same, with PVA-dispersion added, 10%</td>
<td>0.0333</td>
<td>0.0012</td>
<td>(-3\times10^{-7})</td>
<td>2.85</td>
<td></td>
</tr>
<tr>
<td>same, with PVA-dispersion added, 25%</td>
<td>0.0023</td>
<td>0.0004</td>
<td>(-9\times10^{-8})</td>
<td>1.66</td>
<td></td>
</tr>
</tbody>
</table>

The maximum discrepancy between the experimental and estimated values does not exceed 5%, which is recognized as credible for engineering calculations in the field of fire-resistance modeling [17].

Results from Table 1 demonstrated the effectiveness of polymer application, namely the reduction in the washout process by more than 10 times. However, they do not make it possible to fully establish the ratio of retardants to polymers in these compositions and their necessary amount, which requires optimization.

We used a three-factor simplex-central method of planning the experiment in the mathematical software Statistica 12 (developed by StatSoft, USA) to perform optimization of the polymer component of a fire-protection polymeric-inorganic composition at the basic binding agent (a PVA-dispersion) consumption dispersion in the amount of 15, 20, and 25% by weight.

The following factors were chosen as variables: the number of retardants (\(A\)), %, (factor \(X_1\)); the amount of a polymer (PVA-dispersion), %, (factor \(X_2\); their changes are given in Table 3.

The chosen initial parameter was the amount of the washed-out flame retardant in water, whose values were registered experimentally, when the fire-protected specimen was immersed in water (1,000 ml). The experiment planning matrix and its mathematical implementation are given in Table 4.

The result of modeling is the derived regression equation and the constructed ternary surfaces of the output parameter changes depending on changes in the factors of variation (Fig. 3).

Regression equation at the flame retardant’s washout:

\[ Y_{calc} = 2.759 - 0.950X_1 - 0.167X_1^2 + 0.794X_{11} - 1.256X_{22} - 0.075X_1X_2. \]  (4)

The character of change in the isolines for the amount of a washed-out flame retardant on the ternary surfaces is identical; the value directly depends on variations in the concentrations of components of the polymeric-inorganic composition (Fig. 3).
Thus, at PVA-dispersion consumption in the amount of 15% there is a decrease in the amount of a washed-out flame retardant by up to 3 times at a simultaneous increase in the amount of a flame retardant in the composition from 60 to 55% (factor \( X_2 \)). At PVA-dispersion consumption in the amount of 20%, one registers the lowest washout indicator for a flame retardant, which is typical for the composition’s formulation: PVA-dispersions in the amount of 20%; fire retardant – 40%. The character of change in isolines on the ternary surface is analogous to the preceding one. At PVA-dispersion consumption in the amount of 25% the amount of a washed-out flame retardant slightly increases compared to the preceding case; characteristic of the composition’s formulation: a fire retardant – in the amount of 40%; a PVA-dispersion – in the amount of 25%. The character of change in isolines on the ternary surface is analogous to the preceding one.

The result of our modeling is the established lowest ratio of components to protect reed from fire when the washout of a flame retardant is minimal (not more than 1 g), namely for the composition:

- amount of a flame retardant (%) = 30.0...35.0;
- amount of PVA-dispersion (%) = 17.5...22.5.

Results from the study on determining the mass loss by reed samples at ignition, conducted under laboratory conditions, are shown in Fig. 4, and given in Table 5.

Our study has shown (Fig. 4) that the weight loss by the untreated sample amounted to more than 85%; for the sample protected with the modified roofing solution «Skela-i» – about 2.0%. That is, while reed refers to combustible materials, the treated sample of reed withstood the temperature effect and thus refers to the slow combustible materials in terms of mass loss.

As shown by Table 2, it was established during testing of reed samples that the untreated sample ignited on second 52, the flame spread throughout the entire sample in 101 s. In contrast, the sample protected from fire with the roofing impregnating solution, namely a mixture of urea and phosphorus acids and starch («Skela-i») in the amount of 47.1 g/m², did not ignite; the flame did not propagate over the surface, the maximum temperature of flue gases was 101 °C; the flammability index was 0. The same effect was obtained when treating a sample of reed with a composition containing a PVA-dispersion (Table 2).

The obtained results from determining the smallest value in the washout of a flame retardant from a polymeric-inorganic composition make it possible to establish the ratio of retardants to polymers in these compositions and their required amount.

Thus, it was determined that a sample of reed at high temperatures can ignite and rapidly spread the flame over its surface. Treating reed with the modified roofing impregnating solution «Skela-i» prevents to a certain extent the ignition and propagation of flame, but, under the influence of water, the composition is washed out and needs measures able to withstand the influence of moisture.

<table>
<thead>
<tr>
<th>Fireproof reed sample</th>
<th>Temperature of flue gases, °C</th>
<th>Ignition time, s</th>
<th>The time it took for a flame front to travel the sample sections, s</th>
<th>Time to achieve the maximum flue gas temperature, s</th>
<th>Length of sample combustion, mm</th>
<th>Flammability index</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>61</td>
<td>323</td>
<td>52</td>
<td>2 8 7 10 6 8 7 6 7</td>
<td>101</td>
<td>294</td>
</tr>
<tr>
<td>modified roofing impregnating solution «Skela-i»</td>
<td>64</td>
<td>101</td>
<td>–</td>
<td>– – – – – – – –</td>
<td>600</td>
<td>0</td>
</tr>
<tr>
<td>same, with PVA-dispersion added, 20 %</td>
<td>62</td>
<td>103</td>
<td>–</td>
<td>– – – – – – – –</td>
<td>600</td>
<td>0</td>
</tr>
</tbody>
</table>
As regards reed that was protected by the modified roofing impregnating solution «Skela-i» with the addition of a PVA-dispersion, we did not observe the ignition and flame propagation.

Taking into consideration that the reed ignition processes under laboratory conditions may differ from natural ones, in order to establish the effectiveness of fire protection of articles made from reed, the field tests were carried out using certain objects, in particular model samples.

Fig. 5 shows results of testing the untreated reed sample; Fig. 6 – the sample that was treated with the composition «Skela-i»; Fig. 7 – the sample that was treated with the composition «Skela-i» with the addition of a PVA-dispersion.

Fig. 5 shows that the untreated sample of an article made from reed ignited, the flame spread over the entire sample’s area, which led to complete burning.

The results of our tests have established:

– the action of flame on the untreated model of a thermal insulating mat made from reed leads to ignition on second 205 and the flame propagation over the surface, which leads to its complete combustion;
– the model sample of a thermal insulating mat made from reed, treated with protective agents, did not ignite after a model fire based on gasoline had been burned out; accordingly, the flame propagation was not observed. At the same time, we registered the swelling of the protective coating that has reached 3.4 mm and was accompanied by the charring of surface over the area of about 0.025...0.028 m².

6. Assessment of fire resistance of structures made from reed

We estimated effectiveness of the fire protection of a structure made from reed using a technique, which implies determining the efficiency of fire protection (Table 6) from the ratio of burnout rate for the untreated and treated samples.

<table>
<thead>
<tr>
<th>Model sample of thermal insulating mat made from reed</th>
<th>Mass loss Δm, kg</th>
<th>Sample ignition time, s</th>
<th>Area of damage to sample S, m²</th>
<th>Sample burnout speed υ, kg/(m²·s)</th>
<th>Efficiency factor, Eₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>0.820</td>
<td>205</td>
<td>0.196</td>
<td>0.0066</td>
<td>not defined</td>
</tr>
<tr>
<td>treated with the modified roofing impregnating solution «Skela-i»</td>
<td>0.009</td>
<td>not defined</td>
<td>0.025</td>
<td>0.84·10⁻³</td>
<td>7.85</td>
</tr>
<tr>
<td>treated with the modified roofing impregnating solution «Skela-i» with the addition of PVA-dispersion</td>
<td>0.008</td>
<td>not defined</td>
<td>0.028</td>
<td>0.67·10⁻³</td>
<td>9.85</td>
</tr>
</tbody>
</table>
Thus, they are calculated based on the weight loss by a sample and the area of damage to it during testing while simultaneously measuring the time of the sample ignition; combustion characteristics are estimated after testing for flammability based on efficiency factor $E_{ec}$:

$$E_{ec} = \frac{\left(1 - \frac{\tau_1}{\tau_p}\right)}{S},$$  \hspace{1cm} (5)

where $\tau_1$ is the time to ignite an untreated sample; $\tau_p$ is the time to ignite a fire-protected sample; $\upsilon$, $\upsilon_p$ is the burnout rate of untreated and treated samples determined from formula:

$$\upsilon_p = \frac{\Delta m}{\tau_p S},$$  \hspace{1cm} (6)

where $\Delta m$ is the loss of sample weight after testing; $\tau$ is the time of testing (426 sec); $S$ is the area of damage to a sample.

The fire protection efficiency factors $E_{ec}$ calculated from (5), during reed burning, given in Table 6, increase by 8...11 times compared with the untreated ones. Thus, using the proposed technique makes it possible, by an experimental-estimation method, to determine efficiency of the fire protection of a structure made from reed and to improve the reliability of estimation results.

### 7. Discussion of results from determining effectiveness of reed fire protection

The flammability of reed, which is indicated by the research results (Fig. 4–7, Tables 5, 6), is due to its ignition and rapid flame propagation over the surface under the influence of an ignition source and to the weight loss by the sample. In contrast, for a protected sample, due to the effect of fire retardants, the processes of ignition and flame propagation decelerate considerably.

Such a mechanism of the protective agent is predetermined primarily by the decomposition of retardants under the influence of temperature with the absorption of heat and the release of non-combustible gases, by a change in the direction of the material’s decomposition towards the formation of a slow combustible coke residue.

In addition, there occur the processes that slow down the oxidation in the gas and condensed phase with the formation on the surface of wood of a heat-protective layer of coke. This agrees with data reported in papers [5, 6] whose authors also associate the efficiency of thermal protection of a material with the effect from protective substances when adding fire retardants.

In contrast to the research results by authors of [7, 8], our data on the impact of protective agents on the process of heat transfer to a material and changes in heat-insulating properties allow us to assert the following:

- the main regulator of the process is not only the formation of a heat-protective layer of coke, but also the decomposition of retardants with the release of non-combustible gases, in particular nitrogen, carbon dioxide. These gases interact with flame and inhibit the oxidation processes in the gas and condensed phase, which was noted in papers [1, 2];
- significant impact on the process of protecting a combustible material when using a fire-retardant coating is exerted in the direction of reactions in the pre-flame region towards the formation of soot-like products at the surface of the natural combustible material.

Such conclusions can be considered appropriate from the practical point of view, because they make it possible to reasonably approach determining the required formulation for a fire-retardant agent. Treating a material with a roofing composition helps more effectively resist high temperature due to the formation of a heat-insulating layer of coke, which should be emphasized when designing a formulation for coatings made for reed.

From a theoretical point of view, they make it possible to argue on establishing the mechanism of fire protection processes, which are certain advantages of the current study. Specifically, this implies the availability of data sufficient for the qualitative evaluation of the temperature inhibition process and for determining, based on it, the moment at which the process of ignition begins. This would make it possible to investigate the transformation of the surface and structure of reed, treated for fire protection, towards the formation of coke and flame inhibition, and to determine those variables that significantly affect the onset of this process.

Further research could address the theoretical and experimental investigation of combustion processes of heat-insulating materials, establishing a relationship between the components and properties of protective agents and their impact on the processes of heat resistance in building structures.

### 8. Conclusions

1. Patterns in the inhibition of processes of reed ignition and flame propagation over reed, treated with a roofing impregnating solution, indicate the direction of the coating decomposition at high temperature and the formation of a heat-insulating layer of coke, which prevents the burnout and the passage of high temperature to the material. Namely, the fireproof sample, treated with a roofing impregnating solution, did not ignite; the flame did not propagate over the surface; the maximum temperature of flue gases was 101°C; and the flammability index was 0. Adding a PVA-dispersion to the composition in the amount of 20 % reduces the washout process by almost 6 times, while the effectiveness of fire protection does not change. This indicates the possibility of targeted control over the processes of a high temperature transfer to the organic material by using specialized compositions for articles made from reed.

2. The field tests have shown that when exposed to a gasoline flame the untreated model sample of a thermal insulating mat made from reed ignited on second 205, which led to its complete combustion. In contrast, the sample treated with protective agents did not ignite after a model flame exhausted; accordingly, the flame propagation was not observed; in this case, the swelling of the protective coating was registered and the surface exposed to flame was charred over the area of about 0.025…0.028 m².

It was determined that the burnout rate of reed samples, treated with flame retardant agents, reduces by almost 10 times compared to the untreated ones. We have calculated efficiency factors of fire protection at reed burning, which, when compared with the untreated samples, increase by 8...11 times.
References