1. Introduction

Environmentally friendly roof made of reed has been gaining popularity worldwide; in terms of flammability, reed belongs to the group of flammable materials. Fire protection treatment that could reduce the effect of such a drawback makes it possible to provide reed with the capability to resist the action of flame and its propagation.

The means of fire protection impregnate the roof both outside and inside. When dried, a reliable protective coating forms on a surface; it can withstand both rain and snow. Fire protection is effective for a few years and prevents the roof from igniting accidentally when in contact with high-temperature coal (leftovers), firecrackers, and other high-temperature substances.

Basic requirements to protect cellulose-containing materials from fire imply providing them with the ability to resist the action of fire and not to spread flame by the surface. A change in the destruction of a material during fire protection is directed towards the formation of noncombustible gases and difficult-to-fire coke residue, as well as the inhibition of oxidation in the gas and condensed phase.

Building structures have been commonly protected from fire by special coatings, which under the action of high temperature release water; however, they cannot always provide fire resistance. That is why the means have recently been widely applied that are capable to form an insulating layer at the surface of a building structure, which greatly reduces the processes of heat transfer to the material [1, 2].

The use of natural polymeric substances in impregnating mixtures may increase fire protection of a material by forming heat-resistant phases in a protective layer of the coke. That would make it possible to design a new type of flame retardant compositions for building structures, thereby making reed a difficult-to-fire material. In addition, a study into determining the effectiveness of treatment a structure revealed that fire protection ensures a longer ignition process (by 2–3 times) [3, 4].

Given the above, protecting the products made of reed from fire results in certain difficulties when applying the impregnating flame retardants for wood and other building materials. This is due primarily to the fact that the structure and composition of reed differ from them; thus, the process of treatment is not effective and applying the coatings changes the surface.

Therefore, development of protective means for reed, studying the thermal physics of fire protection, the impact of components, which are included in the composition, on a given process, remain the unresolved part of ensuring fire resistance of building structures made of reed and necessitate establishment of the mechanism of fire protection for such materials.
2. Literature review and problem statement

In recent years, several studies that address fire protection have been published, which focus on the synthesis of coatings using inorganic substances, modified with organic compounds capable of forming a coke layer at the surface [5–7]. In most cases, they are modified with polymeric complexes and flame retardants; however, such coatings refer to materials that are easily washed out and are suitable for interior design [6].

The most promising fire-retardant compositions include coatings that swell, which represent complex systems of organic and inorganic components that should exert a combined effect; however, the details are missing [7]. Materials are characterized by high intumescent capacity, but the mechanism of coke formation is not specified, nor the phase and temperature transitions of coatings and coked foam [8].

At present, fire protection is aimed at creating means, which, in the process of heating, form a coke insulating layer of the organic materials at the surface of a building structure [9]. The authors developed an analytical model for the calculation of thermal conductivity of a flame-retardant coating, which takes into account the shape of pores; however, a given model does not account for the way this affects the heat transfer to the structure itself.

Contemporary means create at the surface of materials heat-insulating shields that can withstand the action of fire and must maintain their properties over a preset period [10]. In addition, many coatings have a number of shortcomings, such as the lack of separate components, toxicity of many applied substances at increasing temperature of the environment [11].

Therefore, modeling the thermal conductivity of a flame-retardant coating at swelling, the impacts of components, included in the composition, on a given process is the unresolved part of ensuring fire resistance of building structures; this necessitated undertaking a research in this area.

3. The aim and objectives of the study

The aim of present study is to examine a process of thermal conductivity when protecting a building structure made of reed from fire.

To accomplish the aim, the following tasks have been set:

− to model a process of thermal conductivity of the fire-protected reed under a thermal action on a building structure;
− to establish time patterns in the reduction of thermal conductivity under a temperature influence on a building structure made of reed.

4. Materials and methods to study the front of phase transformations during swelling of a flame-retardant coating

4. 1. Examined materials that were used in the experiment

In order to establish heat conductivity and ignition, we used samples of raw reed and treated reed (Fig. 1):

− with an impregnating solution based on fire retardants (a mixture of urea, phosphoric acids, a natural polymer);
− with a flame-retardant colorless swelling coating (with a composition based on the salts of polyphosphoric acids and a polymer).

![Fig. 1. Model samples of fire-retardant reed: a - raw, b - treated with a fire-retardant impregnating composition; c - treated with a flame-retardant coating](image)

In order to ignite a fire-retardant material, we used the samples of reed of medium size with a diameter to 10 mm and a height of 200 mm, which were treated with the above-described fire-retardant agents.

4. 2. Procedure for determining the indicators of samples’ properties

We applied basic provisions of mathematical physics to conduct a study that involved modeling of the thermal conductivity process of a coating.

To obtain the values of thermal conductivity of the plant raw material, we designed and fabricated special equipment and used a gas burner that simulates a low-calorie source of ignition (Fig. 2).

![Fig. 2. Device for studying the thermal conductivity of reed](image)

A sample of reed treated with a flame-retardant agent was placed in a sample holder and then put into a testing chamber. The sample was fixed so that the end of a thermocouple was pressed against the inner surface of the sample. We ignited a burner and led it to the sample of reed, then measured temperature at the opposite surface. The measured magnitudes were applied to determine thermal-insulating properties and then we recorded changes in the coating.

The criterion for determining thermal conductivity of the flame-retardant coating under thermal action is the formation of temperature at the inner surface of the thickness of reed, which does not exceed the temperature of ignition. In this case, we register the swelling of a coating in the form...
of a layer that resides between the heated environment and the source material.

5. Modeling of the process of thermal conductivity of the wall of reed during swelling of a flame-retardant coating

The result of treatment of cellulose-containing materials with fire-retardant coatings under the action of a heat flow is the change of direction in the decomposition of a material towards the formation of noncombustible gases and difficult-to-fire coke residue. A coke layer formed at the surface is largely capable of absorbing heat and reducing a heat transfer to the material.

Given the above, there is a question regarding the study of thermal properties of a fire-retardant layer of the material under the action of heat.

It should be noted that determining the thermal-physical characteristics of a fire-retardant layer is associated with a number of obstacles, specifically the need to measure temperature in a thin layer of the fire protection (up to 0.5 mm).

In order to establish thermal-physical characteristics of a flame-retardant layer of reed, it is proposed to apply a method for solving the problem on thermal conductivity for a two-component rod with different thermal-physical properties. At the initial period, the external surface of a rod is instantaneously heated to temperature \( T_{\text{h}} \), which is kept constant throughout the entire process of heating, with the distribution of temperature occurring through the coating until reaching a critical temperature of the wall \( T_e \).

Three regions were examined (Fig. 3):

1. outer environment, \( x<0 \);
2. a zone of the swollen layer of coked foam, \( 0<x\leq R \) (\( R \) is the coordinate of the transformation of a coating film into a swollen layer of coked foam, \( h \));
3. material of the sample with a solid substance, \( R<x\leq h \) (\( h \) is a half the thickness of the sample, \( m \)).

Differential equations of heat transfer at the surface of two rods take the form:

\[
a_2 \frac{d^2 T_2(x, \tau)}{dx^2} - \frac{dT_2(x, \tau)}{d\tau} = 0 \quad (\tau>0; \ 0<x<R),
\]

at initial and boundary conditions

\[
T_2(x,0) = T_e, \quad T_2(R, \tau) = 0,
\]

where \( a_1, a_2 \) are coefficients of temperature conductivity of a coating and a material; \( \lambda_1, \lambda_2 \) are coefficients of thermal conductivity of a coating and a material; \( R \) is the thickness of a coating.

Solution to equation (1) and (2) with initial and boundary conditions (3)–(7) is given in paper [10] in the following form:

\[
\theta_1 = \frac{T_1(x, \tau)}{T_e} = \text{erfc}\left(\frac{x}{2\sqrt{a_2} \tau}\right) - \sum_{n=1}^{\infty} \frac{h_n}{x^n} \left( \text{erfc}\left(\frac{2nR-x}{2\sqrt{a_1} \tau}\right) - \text{erfc}\left(\frac{2nR+x}{2\sqrt{a_1} \tau}\right) \right),
\]

where

\[
H = \frac{\lambda_1}{\sqrt{a_1}} \frac{\lambda_2}{\sqrt{a_2}}, \quad R = \frac{1-H}{1+H}
\]

Expression (8) shows the distribution of temperature in a coating with a thickness to 0.5 mm; determining the distribution of temperature throughout thickness is a complex task. Given this, let us consider solution (9), which reflects the distribution of temperature in a material. It was established that at values \( x \sim 0.5 \) the convergence of a series (9) increases and the distribution of temperature is described by the first term with sufficient accuracy [11]:

\[
\theta_2 = \frac{2H}{1+H} \text{erfc}\left(\frac{x-R}{\sqrt{a_1} \tau}\right)
\]

Determining the thermal-physical characteristics of a coating can be performed by applying the following scheme.

Assume that at time \( \tau_1 \) at point \( x=R \) relative temperature is:
\[ \theta_{x=R} = \frac{2H}{1 + H} \text{erfc} \frac{R}{2\sqrt{a_1 \cdot \tau_1}} \]  \hspace{1cm} (11)

and at point \( x=R \) relative temperature is achieved over time \( \tau_2 \) and is equal to:

\[ \theta_{x=R} = \frac{2H}{1 + H} \text{erfc} \left( \frac{x - R + \frac{a_2}{a_1} R}{2\sqrt{a_2 \cdot \tau_2}} \right) \]  \hspace{1cm} (12)

Equating (11) and (12), with respect to the condition that function \( \text{erfc} X \) is unambiguous [10], we obtain:

\[ \frac{R}{2\sqrt{a_1 \cdot \tau_1}} = \frac{x - R + \frac{a_2}{a_1} R}{2\sqrt{a_2 \cdot \tau_2}} \]  \hspace{1cm} (13)

We obtain from equation (13) an expression for determining a coefficient of temperature conductivity of a coating:

\[ a_i = -\frac{a_2 R^2}{\tau_1 (x - R)} \left( \sqrt{\tau_2} - \sqrt{\tau_1} \right)^2. \]  \hspace{1cm} (14)

A value for the coefficient of thermal conductivity is derived by substituting (14) in (11):

\[ \lambda_i = \frac{\lambda_2 \cdot R \left( \sqrt{\tau_2} - \sqrt{\tau_1} \right)}{(x - R) \sqrt{\tau_1} \left( \frac{2}{\theta_2} \text{erfc} \frac{x - R}{2\sqrt{a_2 \cdot (\sqrt{\tau_1} - \sqrt{\tau_2})}} - 1 \right)} \]  \hspace{1cm} (15)

At time \( \tau_1 \) relative temperature at point \( x=R \) is \( \theta_1 \), and at time \( \tau_2 \).

The ratio of these temperatures:

\[ \beta = \left( \frac{\theta_1}{\theta_2} \right)_{x=R} = \frac{\text{erfc} \left( \xi \cdot k \right)}{\text{erfc} k}. \]  \hspace{1cm} (16)

where

\[ \xi = \frac{\tau_2}{\sqrt{\tau_1}}, \quad k = \frac{R}{2\sqrt{a_1 \cdot \tau_1}}. \]

For this case, the calculation equation for a temperature conductivity coefficient will take the form:

\[ a_i = \frac{R^2}{4k^2 \cdot \tau_1}, \]  \hspace{1cm} (17)

and for the coefficient of thermal conductivity, we obtain, by substituting (17) in (11):

\[ \lambda_i = \frac{B \cdot R}{2A \cdot k \cdot \sqrt{\tau_1}}, \]  \hspace{1cm} (18)

where

\[ B = \frac{\lambda_2}{\sqrt{a_2}}, \quad A = \frac{2 \text{erfc} k}{\theta_1}. \]

Thus, we have obtained calculation dependences that make it possible to derive a change in the dynamics of temperature gain by reed surface during swelling of a flame-retardant coating. At the same time, they provide a way to directly calculate the shift in thermal conductivity depending on the effect of temperature.

6. Experimental study into thermal conductivity of plant raw materials during swelling of a flame-retardant coating; and its results

To establish the flammability of reed, we studied the process of its ignition under the action of a burner that simulates a low-calorie source. Results of the study into ignition of raw reed, conducted under laboratory conditions, are shown in Fig. 4.

The study has shown that reed, non-treated with a flame-retardant, under the action of a burner over 5 s, was ignited with flames spreading across the entire surface, leading to its complete burning and the loss of mass.

We then tested the samples that were treated with an impregnating agent and a swelling coating. Experimental study into thermal conductivity of reed during swelling of a flame-retardant agent is presented in Fig. 5, 6.

![Fig. 4. Results of determining the flammability of a reed sample under the action of a burner](image)

![Fig. 5. Test results of reed protected from fire by an impregnating agent: a – effect of flame of the burner on reed; b – formation of a coke layer at the surface of a combustible substance](image)
Fig. 6. Test results of reed protected from fire by a swelling coating: a – effect of flame of the burner on reed; b – formation of a thermally-insulating coke layer at the surface of a combustible substance

Bringing a flame of the burner to the samples of fire-retardant reed led to intensive swelling and a slight rise in temperature at the reverse surface of the sample. The result of the tests conducted helped establish that the swelling of the model sample of reed, treated with an impregnating composition, was above 3 mm; and of the samples, treated with a swelling coating, 4 mm, respectively.

Results of our research into determining the dynamics of temperature of the samples of fire-retardant plant raw materials, conducted under laboratory conditions, are shown in the form of experimental curves, derived according to the above procedure (Fig. 7).

Fig. 7. Dynamics of temperature gain by the inner wall during tests of fire-retardant reed: 1 – treated with an impregnating composition, 2 – treated with a swelling coating

The study has shown that the sample of fire-retardant reed withstood a temperature influence; the action of a heat flow led to the swelling of an impregnation agent and a coating, which lasted for 120 s. At the action of flame of the burner to the sample of reed, protected by an impregnating composition (Curve 1), temperature at the inner surface did not exceed 147 °C, while the mass loss was 2.9 % (Fig. 2). Even greater efficiency was demonstrated by samples that were treated with a coating (Curve 2): T=140 °C, the loss of mass is 2.5 %.

7. Results of determining thermal conductivity during thermal swelling of a coating

Thus, reed with a wall thickness of 0.3÷0.34 mm, a density of 300 kg/m³, has a thermal conductivity coefficient of 0.14 W/(m·°C); its temperature conductivity coefficient is taken to be about 4х10⁻⁷ m²/s [12]; we shall calculate thermal-physical characteristics of a swollen layer of coke.

Fig. 8 shows the calculation of thermal conductivity coefficient λ depending on temperature θ that characterizes the heat-insulating properties of a flame-retardant coating under conditions when part of the heat is absorbed by the coating in order to form a layer of coked foam. Calculation was carried out in line with equation (18), taking into consideration the data on erf c k given in [13].

Fig. 8. Thermal conductivity coefficient dependence on the temperature of heating environment: 1 – a fire-retardant impregnation agent, 2 – a coating

Fig. 8 shows that the rise of temperature leads to an increase in the coefficient of thermal conductivity of the reed wall caused by the loss of water, and then there is a gradual reduction due to the formation of a protective coke layer at the surface. Based on the dependences derived, we calculated thermal conductivity coefficients for fire protection that reaches 1.6 W/(m·°C) for the impregnating composition, and 1.2 W/(m·°C) for the coating, respectively.

Therefore, we have obtained dependences, which make it possible to identify a pattern of the dynamics of fire protection and provide a way to directly determine a change in thermal conductivity for the impregnation of a material and its coating with a protective substance.

8. Discussion of results of studying the process of propagation of the front of phase transformations

When using fire-protection substances to protect reed under the thermal action of a high-temperature flame, based on the research results (Fig. 5, 6), it is a natural process for a coating to swell under the action of temperature with the formation of a protective layer of coked foam, which slow down the processes of thermal conductivity. It is obvious that such a mechanism for the effect of a coating is a factor that regulates the degree of coke formation and the effectiveness of thermal insulation of a material. That agrees well with data given in papers [5, 6] whose authors also attribute the effectiveness of thermal protection on the process of swelling when adding fire retardants. In contrast to results...
from studies [7, 8], the data that we obtained on the influence of a swelling process on the transfer of heat to the material and on a change in the thermal insulating properties, allow us to argue about the following:

– the main regulator of the process is not only the formation of a layer of coked foam, but also the decomposition of fire retardants under the influence of temperature with the absorption of heat and the release of noncombustible gases, retardation of the oxidation process in the gas and condensed phases;
– a significant impact on the process of protection of a combustible material when applying a flame-retardant coating is exerted in the direction of reactions in a pre-flame region towards the formation of ash-like products at the surface of a natural combustible material.

Such conclusions can be considered feasible from a practical point of view, as they make it possible to substantiate the determining of the required formulation of a flame-retardant agent. From a theoretical point of view, they enable determining the mechanism of the processes of fire protection, and these are some of the benefits of our research. The results of determining thermal conductivity of the protected reed (Fig. 7) indicate an ambiguous effect of the nature of a protection substance on a change in temperature. Specifically, that implies the availability of data that are sufficient to qualitatively conduct the process of temperature inhibition and to identify, based on it, a point in time that marks the decline in thermal stability. Such a detection would make it possible to investigate the transformation of a coating surface, which shifts in the direction of an elevated temperature with the formation of coke, and to define those variables that significantly influence the onset of transformation in a given process.

This work is continuation of studies reported in [1–4] with a full description of the mechanism of fire protection for organic natural materials, the formation of coked foam, displacement and execution of thermal insulation of high temperature.

9. Conclusions

1. We have modeled the process of heat transfer during swelling of a flame-retardant coating, determined a coefficient of thermal conductivity, and derived calculation dependences that allow obtaining a change in the dynamics of heat transfer during swelling of a flame-retardant coating. Based on the dependences derived, we calculated thermal conductivity coefficients for fire protection, which reaches 1.6 W/(m°C) for the impregnating composition, and 1.2 W/(m°C) for the coating, respectively.

2. The patterns of inhibition of the process of heat transfer to the material that is treated with a fire-retardant impregnating composition involve several aspects. These include the decomposition of fire retardants under the action of temperature, accompanied by heat absorption and release of noncombustible gases, the inhibition of oxidation in the gas and condensed phase, and the formation of a thermally protective coke layer at wood surface.

In contrast, a coating under the influence of high temperature forms a significant coefficient of swelling, which contributes to the formation of a thermally insulating layer of coke that prevents burn-out and passage of high temperature to the material. This indicates the possibility of targeted control over the processes of temperature transfer by using a flame-retardant agent.

References

1. Introduction

Since the very beginning of its existence, the oil-and-gas industry has had an extremely large negative impact on the environment (soils, geological environment, water resources, atmospheric air). Present-day technologies ensure reduction of the magnitude of anthropogenic impact but this problem still remains unresolved.

Each stage of the life cycle of the oil-and-gas industry facilities is polluting and bringing about high risks of creating irreversible ecologically dangerous consequences for all environment components.