Fire technical properties of intumescent and ablative fire resistant glass

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Abstract Conventional glass materials are weak spots in building fires, and fire codes requires installing fire-resistant glass in specified places. Apart from assessing fire resistance of glass panels by standard tests, there are no universal standards in fire-resistant glass specifications. In standard fire resistance tests, the most relevant performance criteria of fire-resistant glass are integrity, insulation, and radiation. The chemical compositions of the glass products, which depend on the manufacturing method and the required fire resistance standards, are not listed in glass specifications. This article provides an attempt to use calculation method for calculation fire resistance of some types of insulated fire-resistant glass, and describe some specific defects of alkali-silicate gel filled glass. It is shown that recently developed ablative fire resistant glass has some advantage.

Keywords: fire resistant glass, fire resistivity, alkali-silicate gel, ablative hydrogel

1 Introduction
Architectural elements with glass panels are commonly featured in large-scale construction projects. Exterior glass panels have been installed in many new outstanding buildings in cities all over the world. Fire hazard of glass façade of such buildings is a great concern. Conventional glass materials are weak component in case of fire, to improve safety fire-resistant glass has been developed. Apart from assessing fire resistance of glass panels by standard tests, there are no universal or state standards in fire-resistant glass specifications. It should be noted that a glass façade system is comprised of framework, glass, and other accessories. A brief review of fire-resistant glass is presented in this article. In standard fire resistance tests, the most relevant performance criteria of fire-resistant glass are integrity, insulation, and radiation. But in literature, fire-resistant glass can be divided into two categories: noninsulating and insulating. The chemical compositions of the glass products, which depend on the manufacturing method and the required fire resistance standards, are not listed in architectural specifications.

Fire-resistant glass can be defined [1,2] as a glass product that can withstand thermal and mechanical stress during a certain period of time, preventing the spread of fire and combustion products. The product should also satisfy appropriate fire resistance criteria. Standard tests in fire resistance assessment of glass products is controlled by national legislation. In these standard tests, the most relevant performance criteria of fire-resistant glass are integrity and heat insulation. A supplementary criterion of radiation is also specified in national standards such as GOST 30826-2014 and GOST 33000-2014 [2, 3]. These standards mainly control the fire resistance of glass and do not pay attention to durability. Therefore, in
the domestic market presents among high quality glass also a cheap, garage made products. Durability of such product is doubtful and need to be analysed.

The main parameter for using fire-resistant glass is its fire resistance limit. The fire resistance limit is determined under standard test conditions.

National legislation distinguishes two types of fire-resistant glasses:
- Partially insulated glass, ensuring integrity only (E),
- Fully insulated glass, providing integrity, heat insulating ability and limiting heat flux of fire (EIW).

Insulated glasses are of two basic types, i.e. laminated using intumescent interlayers, and ablative gel-filled units. Although they are manufactured using different materials, they are designed with the same objective to provide a glass product which will remain cool on the face opposite the side exposed to the fire [4].

2 Intumescent fire resistant glass

Probably the majority of fire resistant glasses currently in use are laminated glass with interlayers of alkali metal silicate (sodium or potassium) based material. In the case of heating, this substance becomes cloudy, swells up, grows in size and forms a non-combustible foam layer [5].

There is a classic technology to produce fire-resistant glass of this type: on thin layer of glass uniformly poured the solution, the main component of which is sodium or potassium silicate, and dried under special conditions. The process require professional equipment and spacious rooms [6]. Then laminated glass in forming with layers of glass bonded together via the intumescent material layers. These layers expand when exposed to heat from a fire and provide a thick, insulating layer. In general, the greater the overall thickness of the glass, the greater the fire-resistance performance. The heat-insulating properties of such a multi-layered package increase in case of fire: the gel layers successively foam and expand, thus providing high indicators of limiting states for loss of integrity, heat insulating ability and achievement of the limiting value of the heat flux density. The amount of time spent on reaching these limit states is proportional to the number of layers and their thickness [7, 8].

Such glass with silicate intumescent heat insulating layers for the consumer market is offered by Pilkington, the company that first invented and produced a insulated fire resistant glass, and AGS (trade names of Pyrostop and Pyrobel glass, respectively). Later on, Swiss Glass Trösh and the Belgian company Glaverbel, which later became part of AGC, appeared on the market for this product.

In the classic case, the laminated glass is a “sandwich” of 3 mm thick glass sheets with a filling based on alkali metal silicate with a thickness of 1.5 mm. In the Pyrobel glasses produced by AGC there are 2 layers of alcali-silicate that provide fire resistance of 30 minutes and 4 such layers in laminated glass with a fire resistance of 60 minutes.

When the glass is heated above 200 °C, the interlayer material loose transparency, and swells increasing in volume by 5-8 times, forming a solid foam consisting mainly of closed cells. The density of the foam is about 70-500 kg/m3, thermal conductivity 0.07 W/(m*K) [6,10].

The limiting state of laminated glass can be calculated relative to the critical heating temperature under unsteady thermal conditions, taking into account the criterion of glass destruction by temperature on the surface. The solution of the Fourier differential equation under the assumption of uniform heating without regard to relationships with other structural elements and temperature stresses due to uneven heating, has the following form [7]:

\[ T(x,t) = T_{(0,t)} - (T_{(0,t)} - T_{0}) \cdot erf\left(\frac{x}{2\sqrt{\alpha t}}\right) \]  

\[ T(x,t) \] – temperature inside glass at distance x from the surface; Assuming uniform heating, this is any point of the structure, ° C;

\[ T_{(0,t)} \] – surface temperature, °C;

\[ T_{0} \] – initial temperature, °C;

\[ erf\left(\frac{x}{2\sqrt{\alpha t}}\right) \] – Gauss error function (Crump function).
\( x \) – depth of the current layer, m;
\( \alpha \) – coefficient of thermal diffusivity of the current layer \( \text{m}^2/\text{c} \);
\( \tau \) – time of the heating, c.

The fire resistance is calculated from the argument of the error function:

\[
A = \frac{x}{2\sqrt{\alpha \tau}}
\]

(2)

The heating time from (2) is:

\[
\tau = \frac{x^2}{4\alpha A^2}
\]

(3)

Thermal inertia properties vary in proportion to the coefficient of thermal diffusivity, equal to:

\[
\alpha = \frac{\lambda}{\rho c}
\]

(4)

\( \lambda \) – heat conductivity, W/m°C;
\( c \) – specific heat, kJ/kg°C;
\( \rho \) – density, kg/m³.

Reduced thermal diffusivity for multi-layer construction \( \alpha_{np} \):

\[
\alpha_{np} = \frac{\alpha_1 \cdot \delta_1 + \alpha_2 \cdot \delta_2 + \ldots + \alpha_n \cdot \delta_n}{\delta_1 + \delta_2 + \ldots + \delta_n}
\]

(5)

\( \delta_n \) – n-layer thickness.

Consider an intumescent glass consisting of three layers: float glass – alcali-silicate gel – float glass. The total thickness of the glass is 16 mm, of which 3x2 mm is the thickness of the glass, 10 mm is the thickness of the expanded intumescent gel. Similarly, it is possible to calculate the limiting states for a structure containing 2 or 4 layers of gel.

| Table 1. Characteristics of structural elements |
|-----------------------------------------------|
| Variables | Units | Glass | Intumescent filling |
| \( \Lambda \) | W/m°C | 0.93 | 0.07 |
| \( C \) | kJ/kg°C | 0.703 | 0.25 |
| \( \rho \) | kg/m³ | 2500 | 80 |
| \( \alpha = \frac{\lambda}{\rho c} \) | m²/s | 3.410⁻⁷ | 8.210⁻⁸ |

\[
\alpha_{np} = \frac{\alpha_1 \cdot 3 + \alpha_2 \cdot 10 + \alpha_n \cdot 3}{3 + 10 + 3} = 1.7 \cdot 10^{-7}
\]

According to [3] the maximum allowable temperature rise relative to the temperature in the room for fireproof glass is 140 °C.

Initial temperature in the room \( T_0 = +20^\circ \)C.

According to the standard temperature-time curve for the time of fire development (ISO 834), the temperature inside test furnace is:

\[
T = T_0 + 345 \log(8t + 1)
\]

(6)

\( t \) – time in minutes.

According to equation (1)

\[
140 = 1000 - (1000 - 20) \cdot erf\left(\frac{x}{2\sqrt{\alpha \tau}}\right)
\]

\[
erf\left(\frac{x}{2\sqrt{\alpha \tau}}\right) = \frac{1000 - 140}{980} = 0.877
\]
From the Crump function for $\text{erf}\left(\frac{x}{\sqrt{4\pi \alpha \tau}}\right) = 0.877, \ A = 1.54$

In the range of fire resistance from 30 to 90 minutes, the upper value of temperature in the furnace varies from 812 to 981 °C, which corresponds to the range of A value from 1.54 to 1.55. Further, using equation (2) it is easy to determine the fire resistance

This method allows to calculate the limiting fire resistance for fire-resistant glasses filled with alkali metal silicate gel based on the known alternation structure of glass and gel. Table 2 shows the calculation results of the limiting fire resistance of a number of glasses produced by AGC. Glass metrics is based on manufacturer information and author measurement.

| Glass type   | Nominal thickness (mm) | Nominal fire resistivity EI (minutes) | Calculated fire resistivity (minutes) |
|--------------|------------------------|---------------------------------------|--------------------------------------|
| Pyrobelite 7 | 7.9                    | -                                     | 6.4                                  |
| Pyrobelite 12| 12.3                   | -                                     | 15.6                                 |
| Pyrobel 16   | 17.3                   | 30                                    | 30.9                                 |
| Pyrobel 21   | 21.6                   | 60                                    | 48.2                                 |
| Pyrobel 25   | 26.6                   | 60                                    | 73.1                                 |
| Pyrobel 30   | 30.0                   | 90                                    | 93.0                                 |

Intumescent fire-resistant glass produced in a number of companies: - Asahi Glass Co (Japan, Europe, USA), Pilkington (UK), Glass Trösh (Switzerland). The glass sheets made in DLF format size of 3210x2600 mm, packed in wooden box and supplies to processors, where it is cut to size with a diamond saw or water-jet cutting. Intumescent glass is not resistant to UV light, so manufacturers make special version of intumescent glass with an additional UV light filter that. These glasses are characterized by increased thickness due to the additional layer of PVB film. Fire-resistant glass, manufactured by the above mentioned companies, requires high technological culture in processing, transportation and installation. Also, they are among the most expensive.

3 Ablative fire resistant glass

Fire resistant glass based on the ablative principle was invented a few years later than Intumescent glass. Ablative flame resistant glass is a structure of two sheets of tempered glass hermetically separated by a spacer frame, the space between the glasses is filled with a special hydrogel. The principle of the protective action of ablative glass is based on the cooling of the hydrogel due to the latent heat of evaporation of water contained in the hydrogel. The specific heat of water vaporization is 2260 kJ/kg that gives possible to absorb substantial amount of heat. The first patents for ablative flame resistant glass uses acrylamide-based hydrogel without additives. After reaching a temperature above 100 °C, the hydrogel temperature stops growing and remains approximately constant until the end of the evaporation of water contained in the hydrogel. The organic component of the dried hydrogel burns. Therefore, the temperature of the hydrogel surface inside the furnace is also not much higher than 100 °C, which causes a large heat flux and a high evaporation rate [11-12].

The idea of the ablative principle of protecting fire-resistant glasses appeared almost simultaneously with the invention of intumescent glass by Pilkington. The idea is based on the ability of superabsorbing hydrogels to hold a significant amount of water, several times greater than the mass of dry matter. In the event of a fire, the water stored in the hydrogel may evaporate and cool the glass. Pure hydrogel required a large gel layer thickness to provide the desired fire resistance, and the hydrogel based on saline solution caused spacer corrosion even made of stainless steel. The first commercially-produced glass by ablative technology was the product CONTRAFLAM-N1 produced by Vetrotech (Switzerland). A hydrogel containing acrylamide and formaldehyde was used in this product, the spacer frame was made of a titanium profile. Later, this technology began to produce fire-resistant glass in the UK (CGI), in Germany (Hero Fire), Slovenia (Lamiflame), Poland (Glass Team).
Recently there was found that acrylamide has strong neurotoxic and carcinogenic properties, it currently included in the list of extremely hazardous substances. This circumstance proved to be a deterrent in the spread of technology.

In the early 2000s, an attempt was made to find a non-toxic replacement for acrylamide. The gel called PARAFLAM did not have components marked as dangerous. Fire resistant glass PARAFLAM had a number of undoubted advantages, it was durable and resistant to UV light [13].

Figure 1. Comparison of gel thickness for different generation of hydrogel filled ablative fire resistant glass based on fire test results

A problem that prevented the wide spread of fire resistant glass by PARAFLAM was the weak adhesion of the hydrogel to the glass surface. Poor adhesion could lead to delamination on large-sized glasses and fire-resistant glasses in insulated glass unit. Recently, the problem with weak adhesion was solved with introducing of the “two plus” generation hydrogel. The new gel made it possible to manufacture large-size fire-resistant glasses and improve the glass fire resistance [14].

More recent studies have shown that a hydrogel based on a saline solution with a high salt concentration is much more flame retardant. The increase in fire resistance occurs due to two factors. First, there is an increase in heat absorption not only due to the latent heat of evaporation of water, but also due to the latent heat of crystallization of salts. Secondly, the crystallized salt forms a dense heat insulating crust on the surface of the hydrogel, which significantly reduces the flow of heat. As water evaporates, the thickness of the crust grows and its insulating properties grow. Therefore, with an increase in the fire resistance of ablative glass, an ever smaller increase in the thickness of the hydrogel layer per minute of fire resistance is required. With a fire resistance of 60 minutes, the thickness of the ablation and intumescent fire resistant glasses are approximately equal, with greater fire resistance, the ablative fire resistant glass shows a smaller thickness and mass per unit area compared to the intumescent fire resistant glass, with an increase in fire resistance, the gap in the figures grows. For pure acrylamide gel heat flux can be calculated in assumption that temperature of both side of glass does not exceed 100 C. For salt based hydrogel heat flux calculation became more complicated. Therefore, for comparison, we used fire test data available to the authors. Figure 1 shows a comparison of the calculated thickness of a layer of pure acrylamide hydrogel with the actual test data of various samples of fire-resistant ablative glass.

The complexity of manufacturing and the high price of classic intumescent fire resistant glass causes a desire to simplify the process of their production by using equipment for the manufacture resin filled laminated glass. Solution for filling can be made on the basis of liquid sodium silicate (water glass). After pouring, it is necessary solidify the filled solution. In classical intumescent fire-resistant glasses, the solution is poured onto horizontally lying glass and dried under controlled conditions. In order to obtain a layer of solid transparent silicate with a thickness of 1.5 mm, the layer of the filled in solution
must be about 4 mm thick [4]. It is not possible to remove the excess water from the poured laminated glass by drying; one can only try to chemically bind the water molecules with the silicate by polymerizing the solution and forming a solid gel. Indeed, each molecule of silicate during polymerization can bind from one to eight water molecules. In order for the silicon particles to be able to interact with each other, it is necessary either to lower the pH by adding acid, or to reduce the dielectric constant of the aqueous phase by adding inorganic salts or alcohols. The polymerization of sodium silicate solution can be started at elevated temperature. As was shown in [10], the time of gel formation \( t_g \) at a fixed pH value and the chemical composition of the solution is a function of temperature and obeys the Arrhenius law:

\[
t_g = A \exp\left(\frac{E_0}{RT}\right)
\]

where \( E_0 \) is the activation energy, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( A \) is the pre-exponential factor.

In accordance with the Arrhenius equation, the time of gel formation decreases with increasing temperature.

To obtain a flame-retardant glass with silicate gel using a filling technology, it is necessary to hold glass at an elevated temperature to create a solid transparent gel. Polymerization will continue slowly and under normal conditions of use, and glass will become cloudy over time (Figure 2).

**Figure 2.** Delamination of fire resistant glass filled with sodium silicate gel

**Figure 3.** Syneresis in fire resistant glass with a alcali-silicate gel.
After the silicate gel forms and hardens, its structure continues to restructure in a tendency to reach more stable thermodynamic state. As it approaches the equilibrium state, the gel shrinks and displaces the fluid to the periphery (syneresis). It is assumed [9] that syneresis is associated with the formation of new siloxane bonds formed in the process of polycondensation of silanol groups. Siloxane bonds are shorter, occupy less space than two separate silanol groups and lead to gel compression. The syneresis is sensitive to minor changes in the composition of the solution [15]. Silicate gel shrunk, decreasing in size, but retained the original rectangular shape. The separated liquid moved into the periphery and partially leaked out. The glass has lost its flame retardant properties (Figure 3) [5, 10 - 18].

4 Conclusions
In the event of a fire, liquid will leak out through cracks in the glass and the periphery of the glass remains unprotected. Glass may completely fall out of the frame in the first minutes of a fire. If fire-resistant glass has no visible defects (bubbles, delamination) and its sealing is not broken, then it is not possible to visually detect syneresis. How much of the fire-resistant glass installed in fireproof structures with a flooded silicate gel has lost its protective properties as a result of syneresis is unknown. Addition to elevated temperature, there are several other factors (ultraviolet radiation, microwave radiation, phase transitions during freeze thawing) that accelerate the polymerization. All these factors lead to clouding or delamination of the glass.

The specificity of the Russian standards is that they impose fire resistance requirements, but not durability of glasses [18 - 23]. There are durable and short-lived glasses on the market and their comparative analysis is very important from a practical point of view.

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