National University of Science and Technology
Politehnica Bucharest
Faculty of Chemical Engineering and Biotechnologies

DOCTORAL THESIS

Waste glass valorization in materials for passive fire protection

PhD student
Ing. Florentina-Nicoleta Cîrstea

Scientific coordinator
Prof. Dr. Ing. Alina Bădănoiu

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Content

Fire is essential for human activity, but it can cause catastrophes that can lead to loss of life, material destruction and environmental pollution. Fires have become more frequent in recent years and for this reason finding methods that allow limiting their effects represents an important and topical research domain. Special attention must be paid to the fire protection of buildings with steel structures, because the mechanical strengths of these structures are seriously affected when, in the event of a fire, their temperature exceeds 500-600°C.

In this context, the main objective of this doctoral thesis was to obtain materials for the passive fire protection of steel structures, by the valorization of glass waste.

Thus, intumescent paints (organic and inorganic) and magnesium-phosphate coatings with glass waste content were obtained and tested; these materials were applied on metal (steel) substrate to assess their ability to protect it when put in contact with a flame.

The main contributions of this doctoral thesis are presented below.

Intumescent paints were obtained by the addition of inorganic intumescent materials to organic paints based on acrylic / polyurethane / epoxy resins. The inorganic intumescent materials were obtained by the alkaline activation with NaOH solution of a waste glass powder (WGP) with/without various additions (slag, borax, or sodium carbonate).

These coatings were applied on metal (steel) plates to evaluate their behavior when put in contact with a flame; thus, the coated face of the metal plate was placed in direct contact with the flame and the temperature of the opposite face was measured with a digital infrared thermometer.

The main results obtained in this study are:

- ✓ The coating of steel plate with intumescent paints based on acrylic resin with addition of intumescent materials can reduce considerably the temperature of the metal substrate during the direct contact with the flame, compared to those based on epoxy or polyurethane resins. The combinations of 3 or 4 types of intumescent inorganic materials in the composition of paints based on acrylic resin led to a good fire behavior of these coatings, extending the time in which the steel substrate reached the critical temperature;
- ✓ The addition of intumescent materials (42.6%) in the paints based on acrylic resin led to an important increase of the paints' viscosity, as well as to a short shelf life – maximum two weeks after preparation;

- ✓ The use of a smaller amount of inorganic intumescent materials (32.2%) in the composition of the paints based on acrylic resin and the increase of the thickness of the coating applied on metal plate (from 1.75 mm to 4 mm), can delay the initial increase of steel substrate temperature; nevertheless, due to the delamination of the coatings from the steel surface during the contact with the flame, the substrate temperature can exceed the critical value (500-600°C).

The results related to the obtaining and testing of inorganic intumescent paints, based on sodium silicate solution, with the addition of intumescent materials (obtained by the alkaline activation with NaOH solution of soda lime silica waste glass with/without the addition of slag or borax), can be summarized as follows:

- ✓ The substitution of talc, used as a filler in the composition of the reference silicate paint, with intumescent materials, led to the increase of the intumescent coefficient (up to 65%) and to the decrease the activation temperature of this process (intumescence);
- ✓ The studied intumescent coatings effectively protected the metal (steel) substrate when put in contact with a butane flame for one hour and prevented the increase of the temperature of the metal substrate above 600°C;
- ✓ The rate of the temperature increase of the steel substrate was much lower for the coatings containing inorganic intumescent materials as compared to the reference coating (with talc). The application of two layers of the studied coatings and the increase of the applied layer thickness can provide a good protection of the steel support, in case of fire.

The experimental results obtained in the study of the coatings based on magnesium-phosphate cement (MPC) with different additions (WGP, fly ash, organic polymer, expandable graphite) allowed us to formulate the following conclusion:

- ✓ The addition of polymer and/or glass waste powder determines the increase of the MPCs setting time. The substitution of magnesia with WGP (10%) and fly ash (40%) and the addition of polymer, correlated with the increase of the water/solid ratio, determines also the delay of setting time;
- ✓ The thermal treatment performed according to the ISO 834:2019 heating curve (maximum temperature - 1050°C) of magnesium-phosphate binders determined their shrinkage and

mass losses comprised between 25-33%. These changes are correlated with the modification of the mineralogical composition during the thermal treatment; thus, for the MPCs which contain WGP with/without polymer addition, the main process that occurs when the thermal treatment is applied is the dehydration of $KMgPO_4 \cdot 6H_2O$, formed in the reaction between magnesia and monopotassium dihydrogen phosphate solution. For the MPC paste which contain 10% WGP and 40% fly ash, the thermal treatment leads to the formation of forsterite in the reaction of magnesia (which was not entirely consumed in the reaction with the KH_2PO_4 solution) with SiO_2;

- ✓ The values of the compressive strengths of the hardened magnesium-phosphate pastes, before and after applying the thermal treatment, are correlated with the mineralogical composition of the specimens. The reduction of the MgO content (due to its the partial substitution with fly ash and/or waste glass powder) determines a decrease of the compressive strengths (before thermal treatment), correlated with the formation of a lower amount of K-struvite. After the thermal treatment, the compressive strengths increase due to the formation of forsterite;
- ✓ During the contact with the flame of the magnesium-phosphate coatings applied on steel plates, the temperature of the metal substrate is approximately 30% lower than the one recorded on the uncoated steel plate;
- ✓ The adhesion of the studied coatings to the metal (steel) support was very good, without visible delamination of the material layer during and after the contact with the flame.

The effect lightweight aggregates on the properties of studied MPCs was also studied. The lightweight aggregates used in this study were expanded perlite and an aggregate obtained by the thermal treatment of alkali activated waste glass powder – Gt). The obtained results allow the formulation of the following conclusions:

- ✓ The use of above-mentioned lightweight aggregates in the composition of magnesium-phosphate cements (MPCs), correlated with the increase of the water to solid ratio used for the preparation of binder pastes, led to a decrease of the compressive strength, due the increase of the materials' porosity. The adhesion of the coatings to the steel substrate was

very good. The compressive strength of the magnesium phosphate mortars with Gt content were higher as compared with those with expanded perlite;

- ✓ The partial substitution of potassium dihydrogen phosphate (KH_2PO_4) with dipotassium hydrogen phosphate (K_2HPO_4), determined a delay of the MPC's setting time, especially when borax is also present in the system. This substitution determines also the decrease of the compressive strength and coating adhesion to the steel substrate;
- ✓ For the studied MPC coatings, after two successive fire tests (direct contact of the coating applied on steel plate with a butane flame for one hour), the adhesion of the coating to the steel substate remained very good, except for the compositions in which potassium dihydrogen phosphate was partially substituted with dipotassium hydrogen phosphate and the coating thickness was high. The increase of the coating thickness determined a decrease of the steel support temperature;
- ✓ The partial substitution of magnesia with waste glass powder (WGP) in the composition of the studied MPCs and corresponding mortars, as well as the use of WGP for the obtaining of the lightweight aggregate Gt is a viable and environmentally friendly solution for the superior valorization of this type of waste.

The coatings studied in this doctoral thesis can protect steel structures in the event of a fire, extending the time in which the metal reach the critical temperature, thus extending the time in which the steel structure is gravely affected and can lead to the collapse of the building.

This doctoral thesis presents new insights regarding the valorization of various waste (glass, fly ash, blast furnace slag) and is in line with the current requirements regarding the recycling of waste (circular economy) as they are currently defined by European and national strategies.

Keywords: waste glass, intumescent material, organic paint, inorganic paint, magnesium phosphate cement, fire test.

Dissemination of the results obtained in the doctoral thesis

Papers published in ISI journals

1. **Nicoleta Florentina Cirstea**, Alina Badanoiu, Aurelian Cristian Boscornea, Intumescent Silicate Coatings with the Addition of Alkali-Activated Materials, Polymers, May 2022 10;14(10):1937, doi: 10.3390/polym14101937
2. **Nicoleta Florentina Cirstea**, Alina Badanoiu, Georgeta Voicu, Robert Catalin Ciocoiu, Aurelian Cristian Boscornea, Fire Behavior and Adhesion of Magnesium Phosphate Coatings for the Protection of Steel Structures, December 2022, Applied Sciences 12(24):12620, DOI:10.3390/app122412620
3. **Nicoleta Florentina Cirstea**, Alina Badanoiu, Georgeta Voicu, Adrian Ionut Nicoara, Waste glass recycling in magnesium phosphate coatings for the fire protection of steel structures, Journal of Building Engineering, Volume 76, 1 October 2023, 107345, doi.org/10.1016/j.jobe.2023.107345
4. **Nicoleta Florentina Cirstea**, Alina Badanoiu, Aurelian Cristian Boscornea, Influence of intumescent inorganic polymer additions on the fire behavior of paints based on organic resins, U.P.B. Sci. Bull., Series B, Vol. 84, Iss. 4, 2022

Presentation at national conference

5. **National conference presentation -** Alina Badanoiu, Georgeta Voicu, Taha Al Saadi, Oana Cirstea, Adrian Nicoara, **Nicoleta Florentina Cirstea,** Cristian Boscornea, Intumescent materials based on waste glass, Conference CHEMISTY 2020, 27-29 May 2021, Constanta, Romania.