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DOCTORAL THESIS

Alkali activated binder materials with intumescent properties

ABSTRACT

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Content

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Considering the state of the art in the field, at the beginning of this doctoral thesis, the main objectives were:

• Synthesis and characterization of alkali-activated borosilicate inorganic polymer (AABSIP), by alkaline activation of glass waste powder with/without additions of coal ash.

• Investigation of the influence of some compositional parameters (nature, dosage and fineness of constituents) and processing parameters (temperature and curing conditions) on some properties (density, mechanical strength, high temperature behavior, etc.).

• Identification of compositions adequate for the manufacture of intumescent blocks or intumescent coatings to be applied on various supports, for passive fire protection.

The doctoral thesis is structured in two parts.

The first part is a literature review on alkaline activated materials. This study focuses on the materials obtained by alkaline activation of the fly ash [1-7], slag [2, 8, 9] and red mud - waste resulting from the bauxite processing [10-13], with sodium hydroxide as alkaline activator [14-21]. It presents also the synthesis and properties of alkaline activated materials based on glass powder [13, 22].

The second part, structured in 7 chapters, contains personal contributions aiming to develop AABSIPs.

In the first chapter of the second part (**chapter 5**), the materials used in the experimental activity are described, as well as the synthesis methods of AABSIPs. The methods used for the characterization of these materials were: X-ray diffraction (XRD), laser granulometry, scanning electron microscopy (SEM) coupled with EDX, IR spectroscopy, thermal analysis (TG and DTA). Also, specific tests were performed to assess the fire behavior (or at high temperatures), as well as the assessment of mass and volume variations.

The obtained results and their interpretation are presented in the following chapters.

Chapter 6 contains information about the interaction between borax and the alkaline activator (sodium hydroxide solution). To understand these interactions, several pastes have been prepared in which anhydrous borax (A) and hydrated borax (H) were used in different dosages.

The main conclusion of this study is:

- when NaOH solution is mixed with borax (A or H) the system becomes stiffer; the rate of this process depends on the dosage and nature of the constituents;

- the main crystalline compound identified by X-ray diffraction in the pastes obtained by the mixing of NaOH solution with borax is sodium metaborate hydrate;

- SEM images show the presence of phases with a morphology specific to sodium metaborate hydrate.

Some of the information obtained in this study was published in the paper [23].

Chapter 7 presents an extensive study on the influence of some compositional and processing parameters on the main properties of AABSIP systems based on waste glass powder.

The studied parameters were: fineness of the glass powder, dosage and composition of the alkali activator and the dosage borax (H).

The fine grinding of glass waste plays an important role in the synthesis of AABSIP pastes and their behavior at high temperature (intumescent process). A greater fineness of the glass powder (corresponding to a Blaine specific surface of 3000 cm^2/g) led to an important volume increase of AABSIPs, after the heat treatment; a significant increase in volume was achieved - 4 times higher compared to AABSIPs in which the glass powder had a Blaine specific surface of 2100 cm^2/g.

The alkali activator composition (NaOH and/or KOH solution) influences the workability of AABSIP pastes. When only sodium hydroxide was used in combination with the borax (H) and the glass powder, the paste sets and hardens very fast. The use of potassium hydroxide in combination with borax (H) and glass powder resulted in a much slower setting and hardening i.e. the pastes had a much better workability for longer time. The main crystalline compound identified by X-ray diffraction in the hardened AABSIP binders is $NaB(OH)_4\ 2H_2O$, regardless of the alkaline activator composition (NaOH solution with/without KOH).

The studied AABSIPs exhibit intumescent behavior - an important increase in volume and porosity when a heat treatment is applied.

The compressive strengths values of hardened AABSIPs, before to thermal treatment (initial) were between 2 and 14 MPa (and increased with the increase of KOH content in the

alkaline activator composition); the intumescent process that occurs upon heat treatment causes a significant decrease in compressive strength due to the increase of porosity.

Some of the information obtained in this study was published in the paper [24].

Chapter 8 presents information regarding the influence of partial substitution of waste glass powder with another type of waste - coal ash. The substitution of waste glass powder with coal ash (5% and 10% by weight), resulted in an increase of activation temperature of intumescent process with almost 50 °C.

The compressive strengths of the AABSIPs with ash content are lower compared to those based only on waste glass powder, but increased significantly when the heat treatment was carried at 250°C; the occurrence of the intumescent process, which causes the increase of porosity, lead to a decrease of the compressive strength.

Chapter 9 presents data on the use of AABSIPs as coatings for the passive fire protection of various types of construction: steel, expanded polystyrene boards and plasterboard.

The obtained results can be summarized as follows:

- in the case of a steel substrate, the AABSIP intumescent materials may, under certain conditions, maintain the "cold face" temperature (opposite the face were the flame was applied) below 500°C; this temperature is considered critical for the strength of structural steel elements;

- in the case of expanded polystyrene boards, their coatings with AABSIP materials decrease the rate of substrate destruction, thus preventing rapid fire propagation and reducing the risks associated with fire;

- for the plasterboard coated with the studied AABSIPs, an improvement of the fire behavior was found: the rate of propagation of cardboard substrate destruction decreased, as a result of the decrease of the thermal transfer along the length and thickness of the plasterboard, which can prevent fire propagation in adjacent compartments.

Chapter 10 contains an extensive study on obtaining AABSIP mortars and their properties; the AABSIP Mortars were prepared with two types of aggregate: natural- quartz sand and synthetic- industrial waste obtained by mechanical processing of titanium ingots (DSiC).

The main results of this study were:

- the volume increase (intumescent phenomenon) of AABSIPs mortars is lower compared to AABSIPs pastes; these data confirm the important role played by the AABSIPs matrix on the intumescent process;

- partial substitution of the glass powder with coal ash, portland cement or calcium aluminate cement modifies the temperature at which occurs the intumescent process; the substitution of glass powder with 20%wt. calcium aluminate cement, increases activation temperature of intumescent to 700 °C;

- the nature of the aggregate used in the preparation of mortars (sand or titanium waste - DSiC) influences both the intumescent process and the mechanical strengths of mortars; the use of alternative aggregate (DSiC waste) leads to much lower volume increases and a lower mechanical strengths compared to mortars with natural aggregate (sand);

- based on the AABSIPs properties evaluated in this study, a potential use of these materials could be as intumescent blocks (bricks) for passive fire protection in civil and industrial buildings.

Some of the results obtained in this study were published in paper [25].

The last chapter (**chapter 11**) presents results regarding the obtaining and characterization of paints with intumescent filler (AABSIP). The intumescent powder obtained by the grinding of AABSIP paste was dispersed in two types of acrylic binders and a commercial waterborne paint.

The main conclusions are:

- the dosage of AABSIP filler has an important role in the obtaining of effective intumescent paints; the increase of AABSIPs dosage and of the film thickness applied on steel support, intensify the intumescent process (specific for AABSIPs materials) and reduce the temperature increase in substrate;

- the results are promising, but it is necessary to continue this research with the use of a higher AABSIP dosage; also is important to assess the fire behavior of these paints using specific (standardized) tests.

Some of the results presented in this chapter were at the basis of the paper [26].

The last chapter presents the general conclusions.

The main original contributions of this research are:

1) Synthesis and characterization of alkali activated borosilicate inorganic polymers (AABSIP) based on municipal glass waste. Previous researches, reported in the literature, focused on the obtaining of AABSIPs starting from silica fume or fly ash.

2) Use of mixtures of NaOH and KOH solutions (as an alkali activator) in combination with hydrated borax in order to improve the workability of AABSIP pastes.

3) Characterization of AABSIP materials (composition, microstructure, mechanical strength, density) and evaluation of their intumescent behavior. The systematic study of how different compositional and processing parameters influence the properties of AABSIP pastes and mortars.

The studied influencing factors were:

a. composition, nature and fineness of main constituents: fineness of waste glass powder; partial substitution of glass powder with coal ash, calcium aluminate or portland cement; the nature and dosage of the alkali activator; borax dosage; nature of the aggregate used to obtain mortars.

b. curing conditions: time, temperature and humidity of the environment in which the samples were cured.

4) Obtaining and characterization of intumescent coatings to be applied on various substrates (steel plates, plasterboard and expanded polystyrene boards) in order to provide a passive protection against fire. Two types of coatings were studied: inorganic coatings (AABSIP paste) and paintings based on organic binder (acrylic polymers) with intumescent filler (AABSIP).

5) The results obtained in this thesis contributes to moving towards a circular economy by using waste in the production of new, intumescent materials and added value

Dissemination of results

Scientific papers published in ISI Journals

1**. Nicoara, A.I**., Badanoiu, A., Balanoiu, M., Mathias, A., Voicu, G., Alkali activated mortars with intumescent properties, Revista de Chimie, 2019, 70(2), pp. 431-437

2. **Nicoara, A.I.**, Badanoiu, A, Voicu, G., Influence of alkali activator on the main properties of intumescent inorganic polymers based on waste glass and borax, Revista Română de Materiale / Romanian Journal of Materials 2019, 49 (1), 23 – 32

3. Al Saadi, T.H.A., Badanoiu, **A.I., Nicoara**, A.I., Stoleriu, S., Voicu, G., Synthesis and properties of alkali activated borosilicate inorganic polymers based on waste glass, Construction and Building Materials, 2017, 136, pp. 298-306

4. Bărbulescu, L., Bădănoiu, **A., Nicoară**, A., Pîrvu, C., Use of wastes from titanium industry as alternative aggregate for Portland cement mortars, Revista Romana de Materiale/ Romanian Journal of Materials, 2017, 47(1), pp. 16-23

Scientific papers published in journals indexed in international data bases

5. **Nicoara, A.I**., Cirstea, N., Boscornea, C., Badanoiu, A., Coatings with intumescent filler based on alkali activated glass, U.P.B. Sci. Bull., Series B, - accepted for publication

Papers presented at international/national conferences

6. **Nicoară, A-I**, Bădănoiu, A, Voicu, G., Bălănoiu, M., Mathias, A., Synthesis of alkali activated mortars with intumescent properties, 20th RICCCE, Poiana Brașov, 6-9 Sept.e 2017. 7. **Nicoară, A-I**, Bădănoiu, A Voicu, G., Bălănoiu, M., Mathias, A., Alkali activated borosilicate inorganic geopolymers with intumescent properties, 2nd CREMS, Sinaia, 16-18 mai 2017.

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