

INFLUENȚA ACTIVATORULUI ALCALIN ASUPRA PRINCIPALELOR PROPRIETĂȚI ALE POLIMERILOR ANORGANICI INTUMESCENTI PE BAZĂ DE DEȘEURI DE STICLĂ ȘI BORAX

INFLUENCE OF ALKALI ACTIVATOR ON THE MAIN PROPERTIES OF INTUMESCENT INORGANIC POLYMERS BASED ON WASTE GLASS AND BORAX

ADRIAN-IONUȚ NICOARĂ, ALINA-IOANA BĂDĂNOIU*, GEORGETA VOICU

University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science,
Dept. Science and Engineering of Oxide Materials and Nanomaterials, Bucharest, Romania

Intumescent materials have the ability to swell when are subjected to fire or thermal treatment. This type of materials is used for passive fire protection in buildings, providing thermal protection or sealing the penetrations in walls preventing fire spreading in adjacent rooms.

In this paper is presented the preparation of intumescent alkali activated borosilicate inorganic polymers by the alkaline activation of waste glass powder with sodium hydroxide or/and potassium hydroxide solutions and borax additions.

The partial substitution of sodium hydroxide with potassium hydroxide, in alkaline activator composition, improves the workability of fresh pastes, as well as the volume increase during the intumescence process. By fine tuning of various parameters (alkali activator composition, water to solid ratio) is also possible to modify the activation temperature of intumescence process.

Materialele intumescente prezintă o creștere importantă de volum când sunt puse în contact cu flacăra sau sunt tratate termic. Acest tip de materiale sunt folosite pentru protecția pasivă la incendiu a clădirilor, asigurând fie protecția termică a substraturilor pe care se aplică, fie o etanșare a penetrațiilor din pereți (pentru cabluri electrice, țevi etc.) prevenind astfel răspândirea focului în camerele alăturate.

În această lucrare se prezintă obținerea unor materiale intumescente de tipul polimerilor anorganici borosilicatici, prin activarea alcalină a unei pulberi de deșeuri de sticlă cu soluții de hidroxid de sodiu și/sau hidroxid de potasiu și adaos de borax.

Substituția parțială a hidroxidului de sodiu cu hidroxid de potasiu în compoziția activatorului alcalin, îmbunătățește lucrabilitatea pastelor precum și creșterea de volum în timpul procesului intumescent. Prin ajustarea diferiților parametri (compoziția activatorului alcalin, raportul apă:solid) este posibilă modificarea temperaturii de activare a procesului intumescent.

Keywords: Geopolymer, intumescent, fire protection, alkaline activation, waste glass

1. Introduction

Intumescent materials have the ability to swell when subjected to fire or thermal treatment. This type of materials is used for passive fire protection in buildings, providing thermal protection to the underlying surface or sealing the penetrations in walls preventing fire spreading in adjacent rooms [1-5]. Intumescent coatings based on polymers were widely studied in the past thirty years [3], but these materials have some disadvantages i.e. polymers degradation with potential toxic gases release as well as low mechanical properties [5]. Inorganic materials based on hydrated alkali silicates (sodium, potassium or lithium) can be also used as fire protection barriers or coatings [6,7]. The intumescence of these compounds is due to the release of chemically bounded water causing an important swelling – up to 40 times the original volume [7]. This endothermic process determines

also the decrease of the temperature of underlying surface (for coatings) preventing therefore substrate deterioration.

According to Habert and al. [8], industrial production of alkali metal silicates has a major environmental impact, with respect to CO₂ emissions. Therefore, one possible way to produce intumescent eco-friendly materials, with a low carbon footprint, is to use alkali activated materials; these materials, called also inorganic polymers or geopolymers, result by the alkaline activation with concentrated alkalis or alkaline salts solutions of an aluminosilicate source - natural minerals or industrial wastes [8-11].

In the past years, our research group focused on the study of alkaline activation of waste glass powder (WGP) obtained by the grinding of waste glass (cullet) [9-11]. The results obtained so far pointed out the possibility to obtain alkali activated silicate inorganic polymers (AASIP) based on silica-soda-lime glass (WGP) or mixtures

* Autor corespondent/Corresponding author,
E-mail: alina.badanoiu@upb.ro

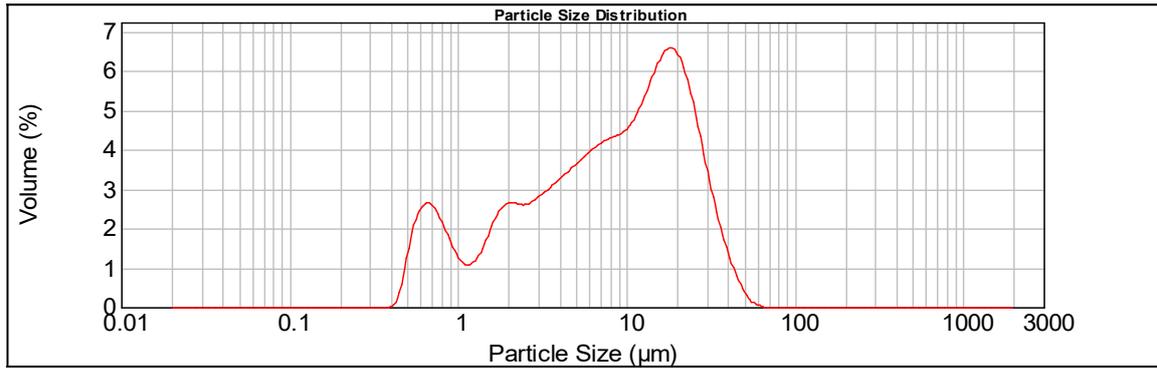


Fig. 1 - Grain size distribution of waste glass powder / Distribuția granulometrică a pulberii de sticlă

Table 1

The compositions of alkali activated borosilicate inorganic polymers / Compozițiile polimerilor anorganici borosilicatici

Specimen	WGP (%wt.)	Na ₂ B ₄ O ₇ ·10H ₂ O (%wt.)	NaOH (%wt.)	KOH (%wt.)	Water to solid ratio (wt.)	(NaOH+KOH) to Na ₂ B ₄ O ₇ ratio (wt.)	WGP to Na ₂ B ₄ O ₇ ratio (wt.)
K_4	58.44	28.14	0	13.42	0.58	0.900	4
Na_4	58.44	28.14	13.42	0	0.58	0.900	4
Na_2	46.71	42.56	10.73	0	0.58	0.476	2
07Na_03K_4	58.44	28.14	9.38	4.04	0.58	0.900	4
07Na_03K_2	46.71	42.56	7.51	3.22	0.58	0.476	2
09Na_01K_4	58.44	28.14	12.08	1.34	0.58	0.900	4
09Na_01K_2	46.71	42.56	9.65	1.08	0.58	0.476	2
07Na_03K_4_030	58.44	28.14	9.38	4.04	0.30	0.900	4
09Na_01K_4_030	58.44	28.14	12.08	1.34	0.30	0.900	2

of WGP and other industrial waste, with intumescent behavior; important volume and porosity increases were achieved when these materials were subjected to thermal treatment at 600-800°C [9-11]. In order to reduce the initiation temperature of the intumescent process, we added borax to these formulations [12], thus obtaining a new class of materials i.e. alkali activated borosilicate inorganic polymers (AABSIP) [13]. The borax addition to NaOH solution, used as alkaline activator of WGP, determines the formation of sodium borate hydrate thus reducing the amount of alkaline activator available for the alkaline activation of WGP; moreover, the workability of the AABSIP fresh paste is affected, and the working time of intumescent binding materials is reduced [12,13]. In this paper we assess the influence of partial replacement of NaOH with KOH in AABSIPs formulations; to the best of our knowledge, we present for the first time the influence of alkali activator composition on the intumescent behavior of AABSIPs based on waste glass powder.

2. Materials and methods

The solid component used for the alkali activated materials synthesis was waste glass powder (WGP) – glass cullet was grinded in a ball mill, up to a fineness corresponding to a Blaine specific surface area of 3000 cm²/g. The grain size distribution of the resulted WGP is

presented in Figure 1; as it can be seen the glass particles sizes are comprised between 0.4 up to 50 µm.

The alkali activator solution was obtained by the mixing with water of NaOH or/and KOH and borax (Na₂B₄O₇·10H₂O) - chemical reagents.

The composition of alkali activated materials (AABSIPs) is presented in Table 1.

Specimens denomination was selected as follows: the composition of alkali activator (N-sodium hydroxide; K-potassium hydroxide; 09Na_01K – mixtures containing 90% NaOH+10%KOH; 07Na_03K - mixtures containing 70% NaOH +30%KOH; WGP to Na₂B₄O₇ ratio - (2;4); water to solid ratio (0.58; 0.3).

The main steps in AABSIPs synthesis were:

- the dissolution of NaOH (or/and KOH) in water followed by the Na₂B₄O₇·10H₂O addition to this solution;

- the resulted solution was mixed with the glass powder, using a mechanical stirrer (800 RPM), for 5 minutes; the paste was cast in molds i.e. cylinders (ϕ = 34 mm and h = 15 mm);

- the pastes were cured at 60°C for 24 hours and then demolded; the resulted specimens were then cured at 20±2°C for the next 7 days;

- after initial curing, the specimens were thermally treated for 60 minutes, in an electrical furnace with a heating rate of 10°C/min, at three temperatures i.e. 250°C, 400°C and 600°C.

The volume and mass variation of AABSIP during the thermal treatment were calculated using equations (1) and (2) [9-12].

$$\Delta V = \left[\frac{V_f - V_i}{V_i} \right] \times 100 (\%) \quad (1)$$

where: V_i = specimen's volume before heat treatment; V_f = specimen's volume after heat treatment.

$$\Delta m = \left[\frac{m_f - m_i}{m_i} \right] \times 100 (\%) \quad (2)$$

where: m_i = specimen's mass before thermal treatment; m_f = specimen's mass after thermal treatment.

The mineralogical composition of AABSIPs, before and after the thermal treatment, was assessed by X-ray diffraction analysis (XRD); this analysis was performed at room temperature using a Panalytical Empyrean diffractometer with $\text{Cu K}\alpha$ ($\lambda = 0.154 \text{ nm}$) radiation, and the scanning was performed between $2\theta = 5 - 65^\circ$.

Supplementary information was obtained by FT-IR analysis; FT-IR spectra were assessed using a Nicolet iS50N spectrometer, at room temperature, using total reflection attenuation (ATR). Sample scans between 4000 and 400 cm^{-1} were performed at a resolution of 4 cm^{-1} .

Thermal analysis was performed on a Shimadzu DTA-TG-50H instrument, in air, in the temperature range: 20 - 600°C with a heating rate of 10°C/min.

The AABSIPs microstructure was assessed by Scanning Electron Microscopy (SEM). SEM images were obtained using a high-resolution electronic scanning microscope equipped with a Schottky emission electron beam (FEI Inspect F50) with a resolution of 1.2 nm at 30 kV and 3 nm at 1 kV (BSE).

3. Results and discussions

During the AABSIPs preparation, it was noticed an increase of the viscosity of the paste resulted by the mixing of the solid component (WGP) with the alkaline solution; the viscosity increase with the increase of the amount of borax added in the solution (Na_2 in comparison with Na_4).

The increase of the paste's viscosity in the systems activated with NaOH and anhydrous borax was previously noticed [12,13] and explained by the formation of sodium metaborate hydrate [12]. As expected, the increase of borax decahydrate amount determines the increase of stiffening rate, most probably due to the formation of an increased amount of sodium metaborate hydrate, from the reaction of borax with sodium hydroxide solution.

The X-ray diffraction analysis performed on the AABSIP specimens with NaOH content, presented in Figure 2, confirms the presence of sodium metaborate tetrahydrate ($\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$) in all AABSIPs.

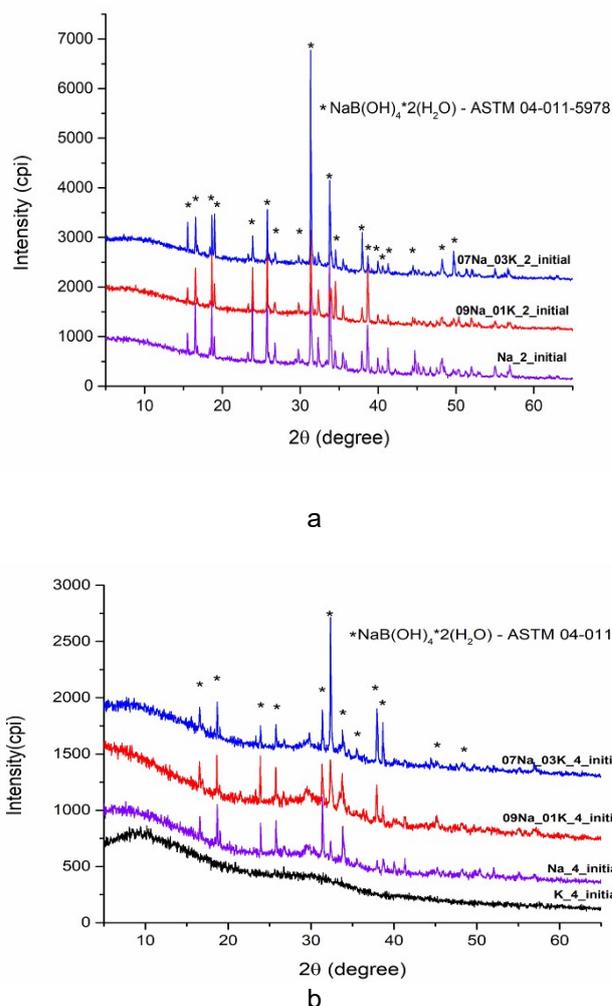


Fig. 2 - X-ray diffraction patterns of AABSIP with WGP to borax ratio of: a - 2; b - 4 / Difractogramele polimerilor anorganici borosilicatici (AABSIP) cu rapoarte diferite pulbere de sticlă/borax: a - 2; b - 4.

As it can be seen in Figure 2a, in the specimens with a higher content of borax (WGP/borax ratio = 2), the main crystalline compound identified by XRD is $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ (ASTM 04-011-5978), regardless of the alkaline activator composition (NaOH with/without KOH solution).

In the compositions with a lower amount of borax (WGP: borax ratio = 4 - Fig. 2b) one can also assess, by XRD, the presence of $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. It is interesting to note the shape of XRD pattern for the specimen activated with KOH+borax solution (K_4) i.e. two wide halos at $2\theta = 5-20^\circ$ and $2\theta = 25-35^\circ$ suggesting the presence of an amorphous phase, specific for the gel like hydrates or/and geopolymeric structures. This halo is also present on the XRD patterns of the specimens activated with mixtures of NaOH+KOH and borax.

One can assume that in these systems, with a lower amount of borax, the amount of

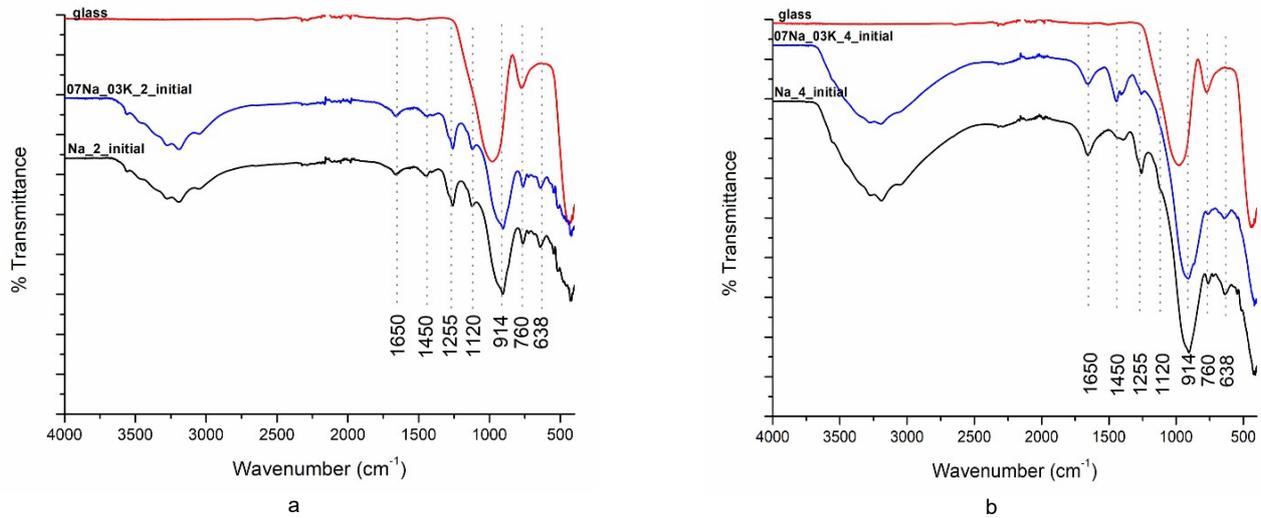


Fig. 3 - FT-IR spectra of AABSIPs with WGP to borax ratio of a – 2; b – 4 / Spectre FT- IR ale polimerilor anorganici borosilicatici (AABSIP) cu rapoarte diferite pulbere de sticlă/borax: a – 2; b – 4

NaOH not consumed in the reaction with borax, is higher and is still available for the alkali activation of WGP. Moreover, in the systems with KOH content, this alkali activator reacts with WGP forming gel like hydrates (geopolymeric gel).

The presence of $\text{NaB(OH)}_4 \cdot 2\text{H}_2\text{O}$ in this type of AABSIP is confirmed also by the FT-IR spectra presented in Figure 3. As it can be seen, all FT-IR spectra contains a broad band located in the 3500 and 3250 cm^{-1} region as well a band at 1650 cm^{-1} which are generally be attributed to the O-H stretching and bending vibrations [14]. These bands correspond to the molecular water present in the structure of sodium metaborate tetrahydrate [15] as well as in gel like hydrates compounds resulted by the alkaline activation of WGP [16].

The bands at 1450 cm^{-1} and 1120 cm^{-1} are attributed to asymmetric stretching of B-O and the bands at 914 cm^{-1} and 760 cm^{-1} are assigned to symmetric stretching of B-O. Also, the band at 1255 cm^{-1} is attributed to B-O-H [15].

On the wide intense band located at 900 cm^{-1} can overlap also the signal specific for Si-O-Si asymmetrical stretching of bridging oxygen within the tetrahedra, from WGP [17].

On the FT-IR spectra of glass powder is present also the band at 750-760 cm^{-1} attributed to Si-O-Si symmetric stretching of bridging oxygen between tetrahedra [17].

This type of AABSIPs, based on WGP activated with NaOH solution with/without borax addition, exhibit an intumescent behavior, as previously reported by our research group [9,11,12]. In order to assess the influence of NaOH substitution with KOH, on the intumescent behavior of AABSIPs, the pastes were thermally treated, for 60 minutes, at 3 different temperatures: 250°C, 400°C and 600°C.

The visual aspect of AABSIPs, before and after thermal treatment, is presented in Table 2.

Table 2

The visual aspect of AABSIPs before and after thermal treatment (tt) / Aspectul vizual al probelor de AABSIP înainte și după tratamentul termic (tt)

Specimen	Before tt,	250°C	400°C	600°C
Na_4				
09Na_01K_4				
07Na_03K_4				
Na_2				
09Na_01K_2				
07Na_03K_2				

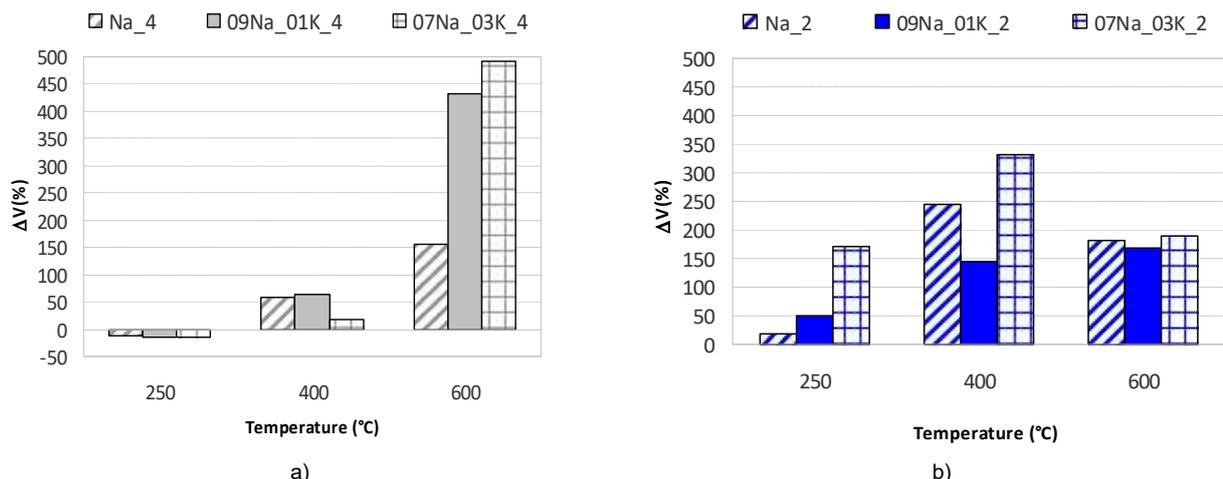


Fig. 4 - Volume changes after thermal treatment of AABSIP with WGP/borax ratio of: a - 4; b - 2 / Modificările de volum, determinate de tratamentul termic, al polimerilor anorganici borosilicatici (AABSIP) cu rapoarte diferite pulbere de sticlă/borax: a - 4; b - 2

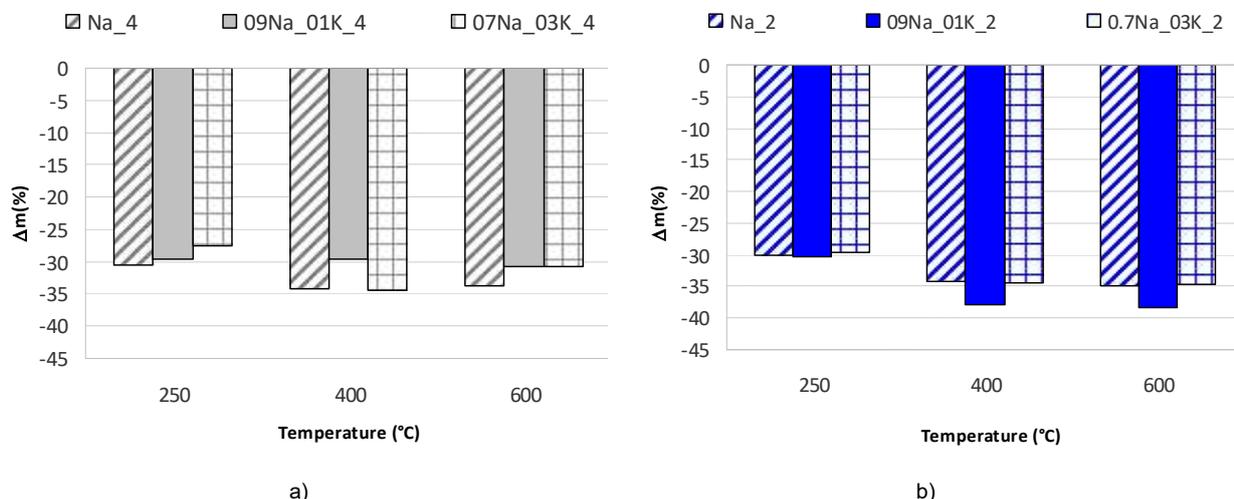


Fig. 5 - Mass losses after thermal treatment of AABSIP with WGP to borax ratio of: a - 4, b - 2 / Pierderile de masă, determinate de tratamentul termic, a polimerilor anorganici borosilicatici (AABSIP) cu diferite rapoarte pulbere de sticlă/borax: a - 4; b - 2.

For the AABSIPs with a lower amount of borax (WGP/borax =4), it can be visually noticed the shrinkage of the specimens thermally treated at 250°C; the further increase of the thermal treatment temperature to 400°C and 600°C, determines an intumescent behavior i.e. an important increase of porosity and volume (see also Fig. 4a). The increase of KOH content (up to 30%) determines an important increase of the volume, especially for the specimens thermally treated at 600°C (Table 2 and Fig. 4a).

For the AABSIPs with a higher content of borax (WGP / borax ratio= 2), the intumescent process starts at a lower temperature i.e. 250°C (Table 2 and Fig. 4b) and the higher volume increase is recorded at 400°C; these data can be explained by the fluxing effect exerted by the higher amount of borax present in these compositions.

The thermal treatment determines also an important mass loss, comprised between 25-35%, for all studied AABSIP compositions (Fig.5).

The increase of borax amount in these systems determines also a small increase of mass loss (Fig. 5b), most probably due to the presence of higher amounts of sodium borate hydrates in these compositions.

In order to better understand the processes which take place during the thermal treatment of AABSIP pastes, complex thermal analysis (TG and DTA) was performed on selected compositions.

Three main endothermic effects were recorded on DTA; these effects are correlated with those present on DTG curves (Fig. 6) and can be attributed to:

- the first effect recorded in the temperature range 20-230°C, results by the overlapping of several effects with maximum at 39°C-125°C; these effects can be determined by the water loss from sodium metaborate tetrahydrate (2 moles of crystalline water [15] - for Na_4 and 07Na_03K_4 compositions) and from sodium/potassium silicate hydrates (physically

bonded water to silanol groups [4]);

- the second effect with a lower amplitude and maximum at 272-290°C can be attributed to the loss of the last two moles of structural water from the sodium metaborate [15] (for Na_4 and 07Na_03K_4 compositions) and also to the loss of ionically hydrated water from sodium/potassium silicate hydrates [4,18];

- the last effect with maximum at 334-367°C can be attributed to the release of structural water i.e. dehydroxylation determined by the condensation of hydroxyl groups bonded to silanol groups [4,18].

It is interesting to note the higher rate of weight loss, recorded on DTG curves, for K_4 as compared with Na_4 and 07Na_03K_4; this can be correlated with the different bond strength of water (or OH⁻) in NaB(OH)₄·2H₂O and gel like alkali silicate hydrates. According to literature data [19], the rate of water (or OH⁻) loss (by a syneresis phenomenon) increases with the increase of cation size i.e. is higher for potassium silicate hydrates as compared with sodium silicate hydrates.

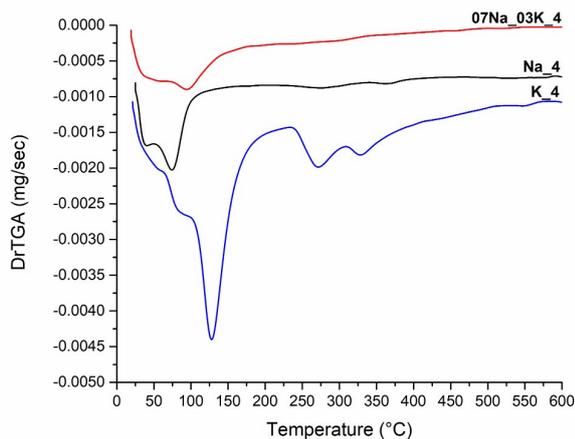


Fig. 6 - DTG curves of AABSIP pastes / Curbele DTG ale pastelor AABSIP.

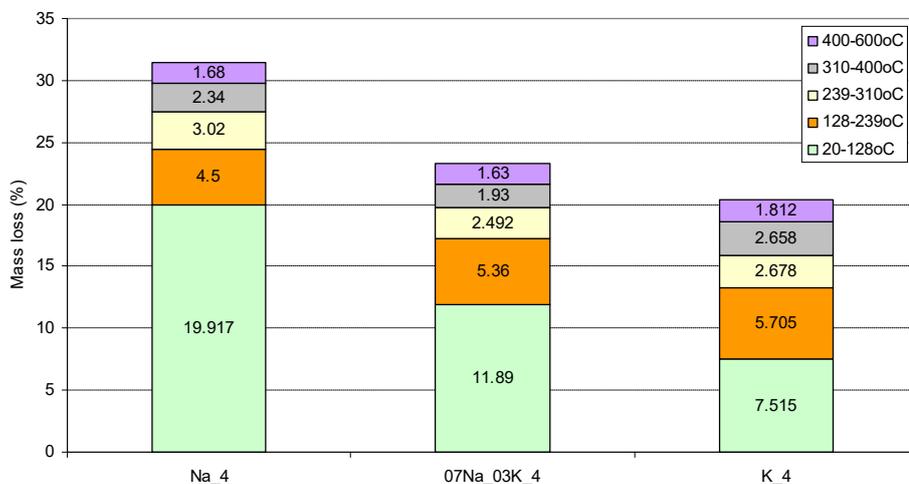


Fig. 7 - Mass losses recorded on TG curves corresponding to different temperature ranges / Pierderile de masă înregistrate pe curbele TG pentru diferite intervale de temperatură.

The water losses recorded on the TG curve, corresponding to the effects previously presented, are shown in Figure 7.

The important weight loss recorded for the AABSIPs with borax content activated with NaOH, in the temperature range 20-310°C, can be explained by the presence of sodium metaborate tetrahydrate; the evaporation of this water (endothermic process) contributes to the consumption of the energy released by an incident fire [4], therefore this material would act as an effective fire protection.

Also, one can notice an increase of mass loss in the temperature range 310-600°C for the K_4 as compared with Na_4; this mass loss is determined mainly by the water loss from sodium/potassium silicate hydrates and confirms the presence of a higher amount of alkaline silicate hydrates in the AABSIP activated with KOH solution. According to literature data [4] the evaporation of water bound in these hydrates determines the expansion (intumescent effect).

Nevertheless, the increase of volume (intumescent process) should be also correlated with the material's viscosity (flowability); the solid amorphous alkali silicate hydrates, with gel like structures, reversibly solidify/soften/flow within a broad temperature range (550-900°C) [20]; therefore in order to obtain the porous structure is also necessary to have an adequate viscosity (flowability) of the material. Although the total mass loss is higher in the AABSIPs with sodium metaborate tetrahydrate, the viscosity (flowability) of the materials is not adequate in order to retain the water vapors generated at lower temperatures.

The SEM analyses (Figs. 8 and 9) confirm also the modification of AABSIPs microstructure during the thermal treatment. The thermal treatment at 250°C does not substantially modify the microstructure of studied AABSIPs, opposite to the thermal treatment at 600°C; in this case big

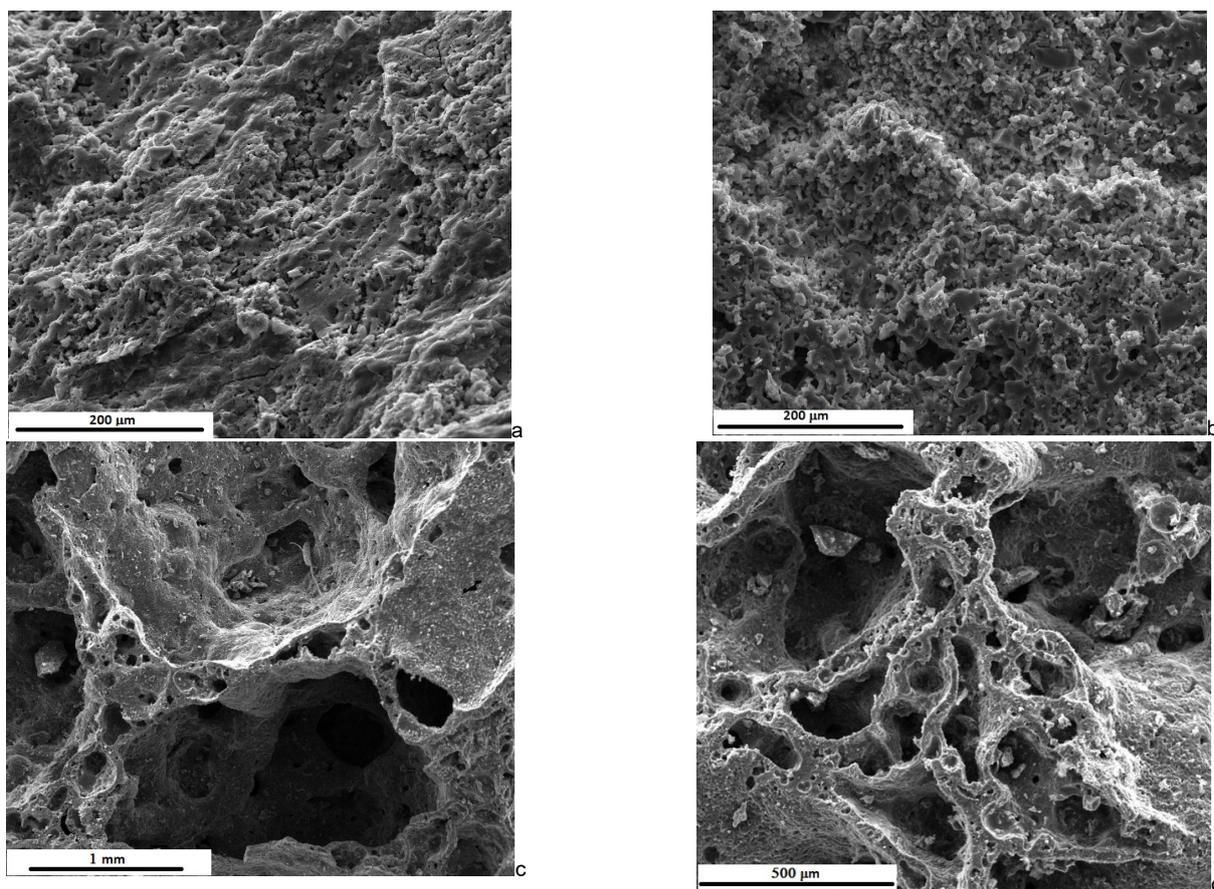


Fig. 8 - SEM images of Na₄ paste: initial (a) and after thermal treatment at 250°C (b) and 600°C (c, d)/Microfotografii SEM ale pastei Na₄: inițial (a) și după tratamentul termic la 250°C (b) și 600°C (c, d).

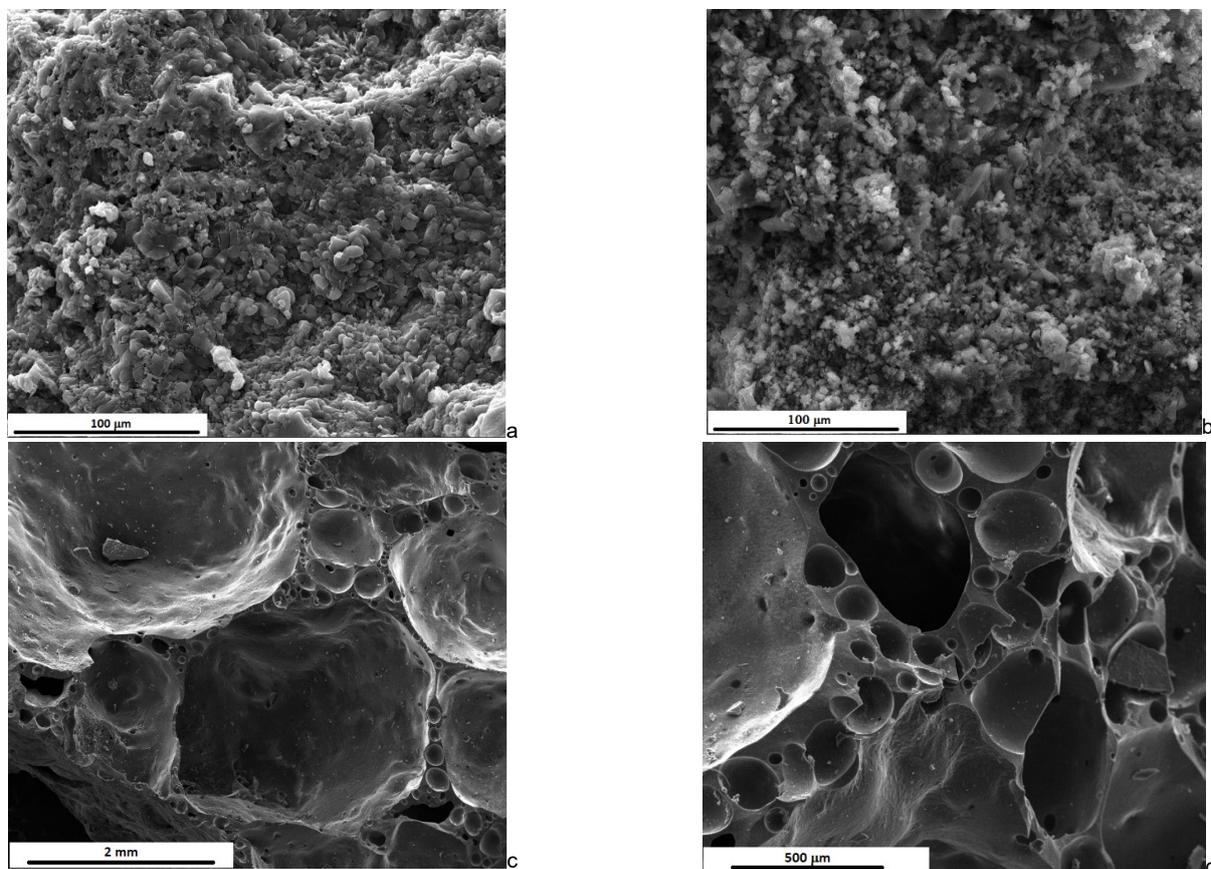


Fig. 9 - SEM images of 07Na₀₃K₄ paste: initial (a) and after thermal treatment at 250°C (b) and 600°C (c, d)/ Microfotografii SEM ale pastei 07Na₀₃K₄: inițial (a) și după tratamentul termic la 250°C (b) și 600°C (c, d).

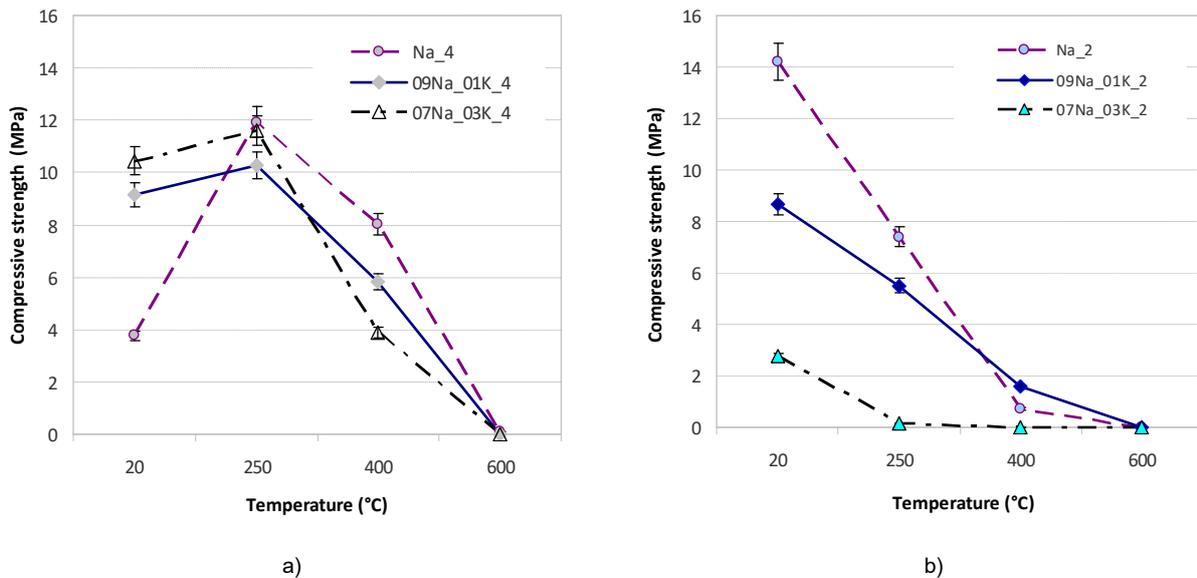


Fig. 10 - Compressive strength vs. thermal treatment temperature of AABSIPs with WGP / borax ratio of: a - 4; b - 2 / *Variația rezistenței la compresiune în funcție de temperatura de tratament termic pentru probele de AABSIP cu raport pulbere de sticlă / borax: a - 4; b - 2.*

pores with various shapes and sizes are highlighted in these materials. One can also assess closed small round pores in the walls of big pores (see Fig. 8 c,d and 9 c,d).

The compressive strength values recorded for AABSIPs, before and after thermal treatment, are shown in Figure 10.

As it can be seen in Figure 10, the compressive strengths of AABSIPs specimens, before thermal treatment (initial) are comprised between 2 and 14 MPa, which are also comparable to some geopolymer pastes based on metakaolin [21]. It is interesting to note the influence of NaOH substitution with KOH in correlation with the borax amount i.e.:

- for lower amounts of borax, the increase of KOH amount determines the increase of compressive strength values (Fig. 10a); this trend was also observed in a previous study for alkali activated materials based on CRT glass [22] and can be explained by the stabilization of large silicate oligomers and extend of the geopolymerisation process in the presence of large cations such as K ions [23];

- for higher amounts of borax, the higher value of the compressive strength is recorded for the composition activated with NaOH (Fig. 10b); this can be due to the formation, in this system, of a higher quantity of sodium metaborate tetrahydrate which can contribute to the increase of the mechanical properties [22, 24].

For the AABSIPs with a lower amount of borax (Fig. 10a) the thermal treatment at 250°C determines the increase of compressive strengths values, in good correlation with volume contraction (Fig. 4a); the further increase of the thermal treatment temperature determines the

important decrease of the compressive strengths due to the volume and porosity increase (see also Figs. 8 c,d and 9 c,d).

For the composition with a higher amount of borax (Fig. 10b) the increase of the thermal treatment temperature determines the decrease of compressive strength values; the AABSIPs thermally treated at 600°C do not have recordable values of the compressive strengths.

The above reported results suggest the possibility to use these AABSIPs as intumescent fire-retarding materials. In order to obtain an adequate consistency for this material to be used as a sealing paste (putty), we prepared also compositions with a lower water to solid ratio (0.3) (Table 1).

The mass and volume changes of thermally treated AABSIPs, prepared with a lower amount of water are presented in Figure 11.

As it can be seen in Figure 11a, the mass losses recorded for the AABSIPs prepared with a smaller amount of water (water/solid=0.3) are slightly lower as compared with those assessed for the AABSIPs prepared with greater water to solid ratio (0.58). Also, the volume increase recorded at 600°C, decreases with the decrease of water to solid ratio. This was to be expected, because the main phenomenon which determines the swelling of this type of materials is the gradual removal of water (or OH⁻) from the formed hydrates; nevertheless, the volume increase is still high i.e. 250-300% (Fig. 11b).

The decrease of water content in AABSIPs determines, as expected, the increase of compressive strengths, before and after thermal treatment at 250°C and 400°C (Fig. 12).

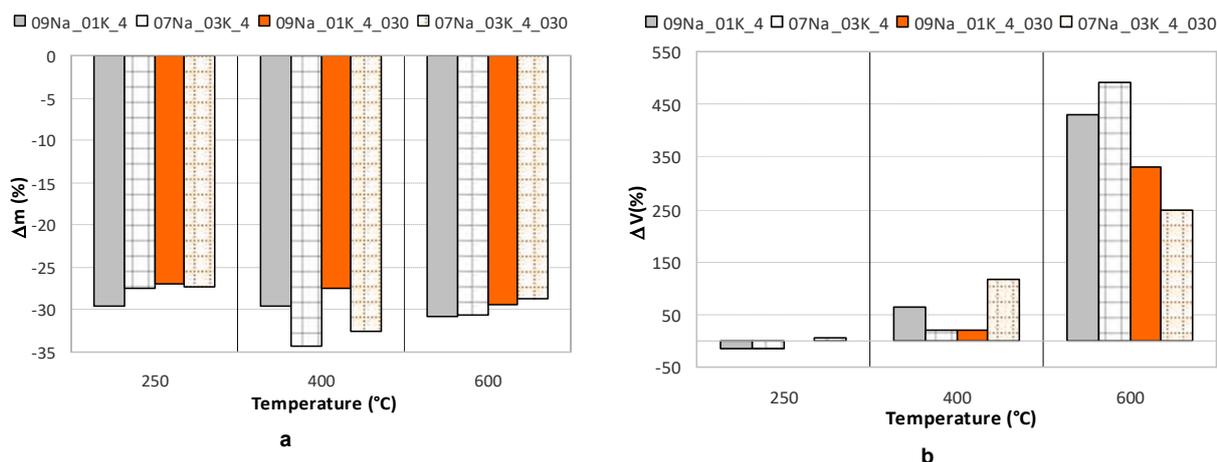


Fig. 11 - Mass (a) and volume (b) changes vs. thermal treatment temperature of AABSIPs with various water to solid ratios (0.58 and 0.3) / Modificările de masă (a) și volum (b) determinate de tratamentul termic la diferite temperaturi al pastelor de AABSIP preparate cu diferite rapoarte apă / solid (0.58 și 0.3)

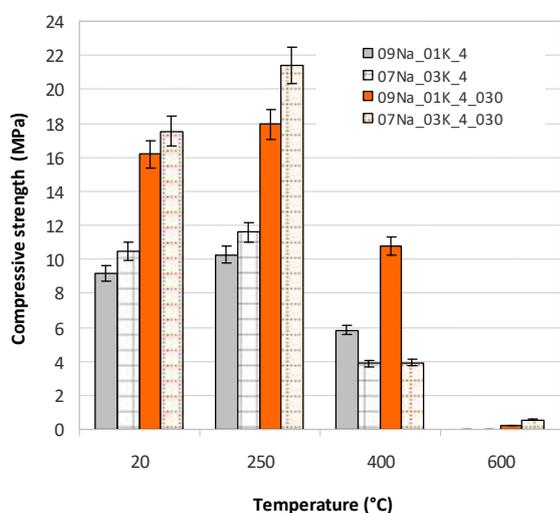


Fig. 12 - Compressive strengths of AABSIPs with various water to solid ratios, after the thermal treatment at different temperatures / Rezistența la compresiune a pastelor de AABSIP cu diferite rapoarte lichid/solid, după tratamentul termic la diferite temperaturi.

4. Conclusions

Intumescent materials (AABSIPs) can be produced by the alkaline activation of waste glass powder (WGP) with NaOH or/and KOH solutions and borax additions.

The main crystalline compound identified by XRD in AABSIPs is $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, regardless of the alkaline activator composition (NaOH with/without KOH solution). In the compositions with a lower amount of borax (WGP/borax ratio = 4) activated with KOH and mixtures of KOH and NaOH is also present an amorphous phase, specific for the gel like hydrates or/and geopolymeric structures.

The studied AABSIPs exhibit intumescent behavior i.e. important increase of volume and porosity, when subjected to thermal treatment. For the AABSIPs with a lower content of borax (WGP/borax =4), the intumescence process is

first recorded for the specimens thermally treated at 400°C and increase with the increase of temperature up to 600°C. The increase of KOH content (up to 30%) in alkaline activator solution, determines an important volume increase, especially for the specimens thermally treated at 600°C, most probably due to the higher amount of gel-like sodium/potassium silicate hydrates formed in this composition. For the AABSIPs with a higher content of borax (WGP/borax ratio= 2), the intumescent process starts at a lower temperature i.e. 250°C and the bigger volume increase is recorded at 400°C.

The compressive strengths values of AABSIPs, before thermal treatment (initial), range from 2 to 14 MPa. As expected, the intumescent process, determines an important decrease of the compressive strength due to the increase of porosity.

The results presented in this paper highlight the possibility to obtained intumescent materials, based on waste glass powder, with various intumescence activation temperatures and important volume increases (high foaming pressures), by fine tuning of alkali activator composition.

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