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Alternative alkali activators based on waste bottle glass and waste cathode-ray tube glass

ALTERNATIVE ALKALI ACTIVATORS BASED ON WASTE BOTTLE GLASS AND WASTE CATHODE-RAY TUBE GLASS

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SUMMARY: Alkali-activated binders are an environmentally friendly alternative to Portland cement, particularly when locally-available raw materials are used. It is well known that alkali activation with a sodium silicate activator generates a hardened binder with higher compressive strength than a binder hardened with sodium hydroxide. As the alkali-silicate activators are produced through energy extensive processes, and their use can significantly increase the carbon footprint of the final products, it is of great significance to develop alternative alkaline activators based on locally-available waste materials. This article assesses the potential to apply waste bottle glass and waste cathode-ray tube (CRT) glass to synthesise alternative alkali activators by the hydrothermal method. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was used to determine silicon and aluminium content in the alternative activators. The influence of dissolution process parameters (time, temperature, particle size) on the concentrations of silicon and aluminium in the alternative activators was investigated. The alternative activators with silicon concentration up to 19 g/L and aluminium concentration up to 0.9 g/L were prepared at $T = 120\text{ }^{\circ}\text{C}$ and boiling time 24 h. The alternative alkali activators and, for comparison, also commercial sodium silicate were used in the alkali activation of fly ash powder. The formed pastes were cured at $70\text{ }^{\circ}\text{C}$ for 72 h. Mechanical strength measurements indicated that alkali activation of fly ash with the optimal alternative activator yielded hardened paste with compressive strength of 33 MPa. However, the compressive strength of hardened paste prepared from fly ash and commercial sodium silicate reached 70 MPa. Part of this difference can be ascribed to the lower density of hardened pastes prepared with alternative activators.

KEYWORDS: alkali-activated materials, alternative alkali activators, waste bottle glass, waste cathode-ray tube glass, fly ash, hydrothermal method.

1 INTRODUCTION

Alkali-activated binders are cement-like materials produced by mixing (partially) amorphous aluminosilicate precursors and alkaline aqueous activators (mostly sodium/ potassium silicate and sodium/ potassium hydroxide). Suitable precursors for alkali-activated materials (AAMs) are thermally activated clay, natural pozzolan (e.g. volcanic ash), as well as different kinds of industrial wastes, such as fly ash, bottom ash, and various slags [1]. The main environmental benefit of using wastes as precursors instead of natural materials is the reduced carbon footprint of alkali-activated materials [2].

The production of silicate activators (water glass) contributes significantly to the carbon footprint of alkali-activated materials. Therefore, the number of studies focusing on finding or producing activators from waste materials has increased [3]. One such material is waste glass, for which it has been shown in a few recent publications that, in combination with hydroxides, can be an adequate substitute in a certain case for the water glass [4, 5]. Waste glasses can be used in two ways for alkali activation: as a solid precursor for the alkali-activated material and/or as a raw material for producing low-cost sodium silicate solutions used as alkali-activators [4, 6, 7]. Municipality waste glasses were used to produce sodium silicate solutions with "dissolution" in NaOH/Na₂CO₃ solutions [8]. These alternative alkali activators were applied for synthesising binders based on alkali-activated slag [9] and alkali-activated fly ash with similar compressive strengths to binders prepared with commercial sodium silicates [10]. Biomass-derived substitutes for water glass have also been recently used [11].

Within the present study, attempts have been made to obtain the alternative activators from waste glass and waste cathode-ray tube glasses by hydrothermal method and verify their efficiency in the synthesis of alkali-activated materials. Furthermore, the substitution of industrial water glass in the formulation of alkali-activated materials obtained from fly ash was evaluated.

2 MATERIALS AND METHODS

Waste bottle glass (BG) and cathode-ray tube glass (CRTG) were used to synthesise alternative alkali activators. Bottle glass and cathode-ray tube glass were milled, homogenised and sieved to a particle size below 25 μm , 63 μm and 90 μm . As a precursor for the preparation of alkali-activated binders, fly ash from a Slovenian thermal power plant was used.

A sequential X-Ray Fluorescence (XRF) Spectrometer (ARL PERFORM'X, Thermo Fisher Scientific Inc., USA, UniQuant software) was used to determine the chemical compositions of the raw materials. Before the measurement, powder samples were heated at 950 °C and then fused beads were prepared at 1050 °C – 1100 °C by commercially available flux composed of 50 % lithium tetraborate and 50 % of lithium metaborate (FX-X50-2, Fluxana GmbH & Co. KG, Germany). The mass ratio of powder to flux was 1:10.

The specific surface area of the powders was determined by nitrogen sorption (ASAP 2020, Micromeritics, Norcross, USA) at the temperature of 77K in the relative pressure range between 0.05 and 0.3. Before each measurement, the powders were heated to 70 °C–105 °C for at least 3 hours and degassed to 10^{-3} Torr (Flowprep equipment, Micromeritics, Norcross, GA, USA). The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The particle size of the powders was measured with a laser-scattering particle size distribution analyser (LA-920, Horiba Jobin Yvon, France).

Chemical composition and BET surface areas of raw materials are shown in Table 1. Bottle glass contains 72.4 wt. % of SiO_2 and 0.91 % of Al_2O_3 . Cathode-ray tube glass contains 58.5 wt. % of SiO_2 and 2.07 % of Al_2O_3 . Fly ash contains 44.8 wt. % of SiO_2 and 23.0 wt. % of Al_2O_3 and, as reported previously [12], the mass percentage of amorphous phase in fly ash was 78.7 %. The specific surface area of fly ash was 2.85 m^2/g .

Table 1: Chemical composition (wt. %, XRF) and specific surface area of raw materials

Oxide [wt. %]	waste glasses for the preparation of alternative activators		solid precursor
	bottle glass (BG)-90 μm	CRT glass (CRTG)-90 μm	fly ash
LOI 950°C	/	/	0.51
Na_2O	13.47	7.61	1.19
MgO	1.68	0.46	2.80
Al_2O_3	0.91	2.07	22.98
SiO_2	72.37	58.49	44.82
K_2O	0.73	7.35	2.20
CaO	10.07	1.15	12.38
Fe_2O_3	0.21	0.16	10.65
BaO	0.07	7.72	0.08
PbO	0.06	3.92	/
BET surface area [m^2/g]	0.45	0.53	2.85

The measured particle size distributions of the milled and sieved bottle glass and CRT glass powders are presented in Fig 1. As shown, the glass powders sieved through a 90 μm -sieve have trimodal particle size distributions with two broad maxima at 3.5 μm and 20 μm and one sharp maximum at 67 μm . The bottle glass powder sieved through a 63 μm -sieve has also trimodal particle size distribution with three broad maxima at 3.5 μm , 17 μm and 45 μm . The CRT glass powder sieved through a 63 μm -sieve has a bimodal distribution with two broad maxima at 3 μm and 15 μm . Both glass powders sieved through a 25 μm -sieve have bimodal particle size distributions with one broad maximum at 4.5 μm and one sharp maximum at 10 μm . The mean particle sizes of glass powders are presented in the table in Figure 1.

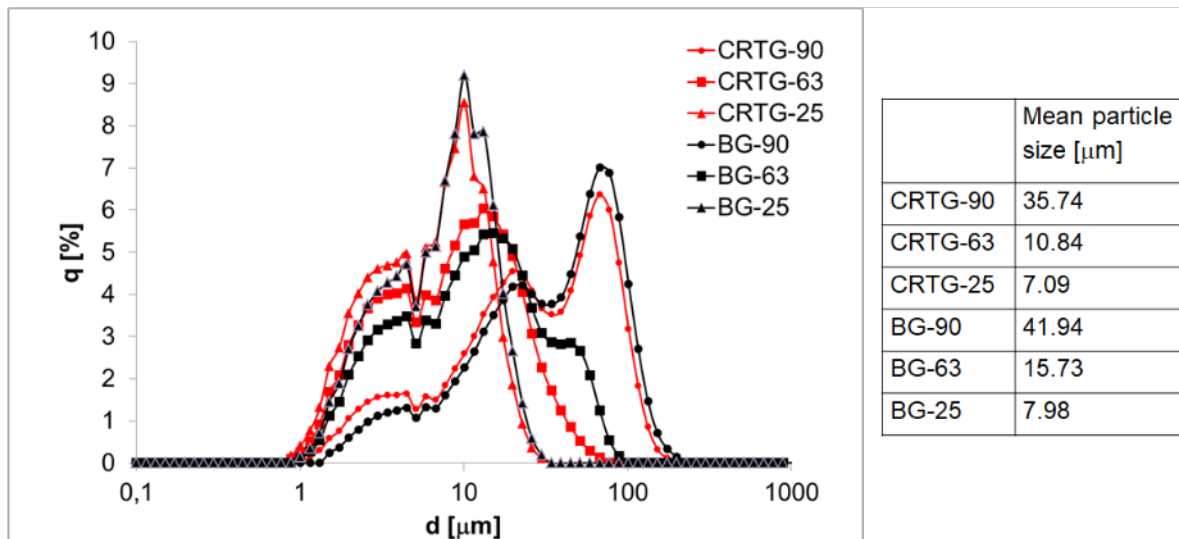


Figure 1: Particle size distribution and mean particle size of milled and sieved bottle glass and CRT

To synthesise alternative alkali activators, 20 g of the waste glass powders were added to 200 mL of 10 M sodium hydroxide solution. Distilled water and NaOH flakes (Donau Chemie AG, Austria) were used to prepare a 10 M NaOH solution. The suspensions were left boiling for 4 hours to 45 hours at constant mixing with a magnetic stirrer. The suspensions were then cooled down and filtered. The obtained filtrates were analysed for silicon and aluminium content by inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian, Model 715-ES) and were later used as alternative activator solutions in alkali activation of fly ash. As reference alkali activators, 10 M sodium hydroxide and commercially available sodium silicate solution (Na₂O; 15.4 %, SiO₂; 30.4 %, H₂O; 54.2 %, Crystal 0112, Tennants Distribution Ltd, United Kingdom) were used. The mass percentage of fly ash in the pastes was from 73 % to 80 %; the mass ratio of liquid to solid was from 0.25 to 0.32. The composition of binder pastes is presented in Table 2.

Table 2: Composition of binder pastes, presented as mass percentages of components [%]. The mass ratio of liquid to solid (L/S) is presented as (mass of liquids)/ (mass of solids) [/]

Binder formulation	Fly ash [%]	Water glass (Na ₂ SiO ₃) [%]	Alternative activator (BGA or CRTGA) [%]	solid NaOH [%]	10 M NaOH [%]	The mass ratio of liquid to solid (L/S) [/]
73.2FA24.4NS2.4NaOH(s)	73.2	24.4	/	2.4	/	0.32
80FA8.8NS11.2BGA-24h	80	8.8	11.2	/	/	0.25
80FA8.8NS11.2CRTGA-24h	80	8.8	11.2	/	/	0.25
80FA8.8NS11.2NaOH(aq)	80	8.8	11.1	/	11.2	0.25
77FA23BGA-24h	77	/	23	/	/	0.30
77F23CRTGA-24h	77	/	23	/	/	0.30
77F23NaOH(aq)	77	/	/	/	23	0.30

The pastes were manually mixed for 2 minutes and then moulded into prisms of 80 x 20 x 20 mm³. The pastes were then cured at a temperature of 70 °C for 72 hours in a heating chamber. The hardened binders were then demoulded, and mechanical strength was measured. The mechanical strength (compressive and bending strength) was determined using a compressive and bending strength testing machine (ToniTechnik ToniNORM, Berlin, Germany, force application rate 0.05 kN/s). The bending strength of the mix compositions was assessed under three-point bending (TPB) loading. The compressive strength was assessed under compression loading using the two broken portions from the bending test. The

reported bending strength values represent the average results obtained from 3 test specimens of dimension (20 × 20 × 80) mm³. The reported compressive strength values represent the average results obtained from 5 test specimens.

The microstructures of the hardened binders were observed at polished cross-sections in a scanning electron microscope (SEM; JEOL JSM-IT500 LV, Tokyo, Japan). SEM was equipped with an energy-dispersive X-ray spectrometer (EDS, Oxford Instruments) coupled with Aztec software for the quantitative analyses of elemental compositions. Before SEM scanning, the specimens were vacuum-dried at 40 °C in a vacuum drier.

3 RESULTS AND DISCUSSION

3.1 The concentration of silicon and aluminium in the filtrates

The diagram in Figure 2 shows the concentration of dissolved silicon (2a) and aluminium (2b) as a function of dissolution time for waste glass powders sieved through a 90-micrometre sieve. It is evident that the concentration of silicon and aluminium first increases with dissolution time for both activators, but when a longer dissolution time was applied (45 h), the concentration of both silicon and aluminium decreased. The concentration of silicon in the activator sourced from bottle glass (BGA) was higher than the concentration of silicon in the activator sourced from CRT glass (CRTGA) when dissolution time was 4 h and 24 h. The concentration of dissolved aluminium was approximately the same in both activators after 4 h of dissolution, while after a longer dissolution process (24 h and 45 h), the concentration of aluminium was higher in the CRTG activator. The concentration of aluminium in the BG activator was less than 10 mg/L after 45 h dissolution. It is logical from consideration of higher silicon oxide content in bottle glass than in CRT glass that the concentration of silicon is higher in the BG activator than in the CRTG activator. However, when the dissolution time was 45 h, the Si concentration was higher in the CRTG activator than in the BG activator. The BG activator could be supersaturated after a certain amount of dissolution time [13], then the formation of aluminium- and silicon-containing solid compounds could occur, and they could be removed during the filtration. Decreasing the concentration of silicon and aluminium can also be explained by the accumulation of ions on the surface that disable or slow down the dissolution process.[14]

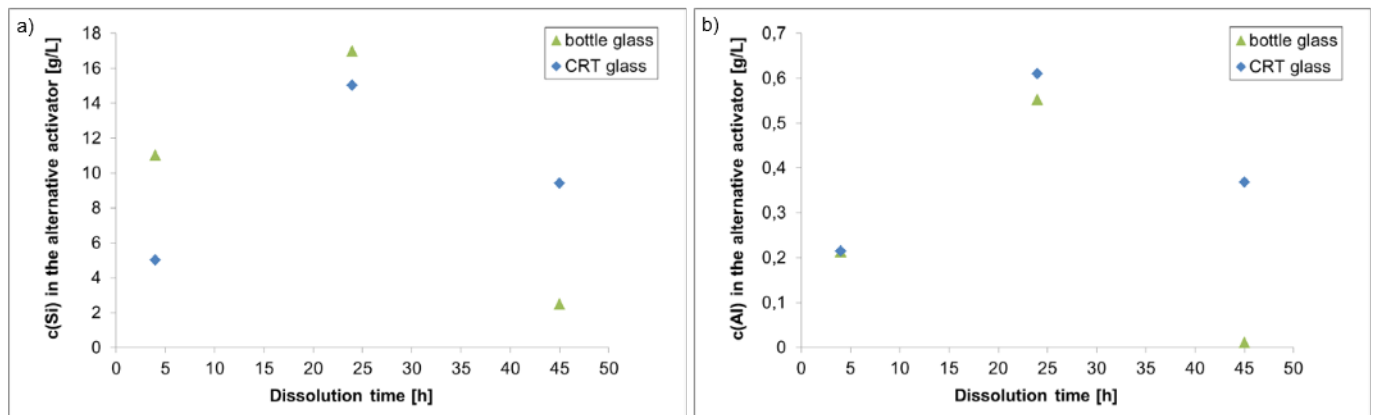


Figure 2: The concentration of a) silicon (c(Si)) and b) aluminium (c(Al)) as a function of dissolution time.

Figure 3 shows the concentration of silicon (3a) and aluminium (3b) in the BG- and CRTG activator solutions as a function of the mean particle size of glass powders in the 45 h-dissolution processes. The concentration of silicon and aluminium in the BG activator increased with decreasing glass particle size. Smaller particles have a larger specific surface area, and there is a greater exchange of ions of the solvent and glass particles; the solubility of silicon oxide in the smallest bottle glass particles was the highest. It seems that 45 h-contact of larger bottle glass particles and 10 M sodium hydroxide resulted in the dissolution of other bottle glass components that readily formed solid compounds with silicon. The precipitated particles were subsequently filtered away, and consequently, the silicon concentration in the activator was low. This trend was not observed in the dissolution process of the CRTG activator, where the concentration of silicon was not so dependent on the particle size. Regardless of decreasing the particle size of CRTG, the concentration of silicon in the CRTG activator was in the range of 8.5 g/L to 11 g/L (at dissolution time 45 h). On the contrary, aluminium concentration in the alternative activator prepared from CRTG decreased with decreasing particle size.

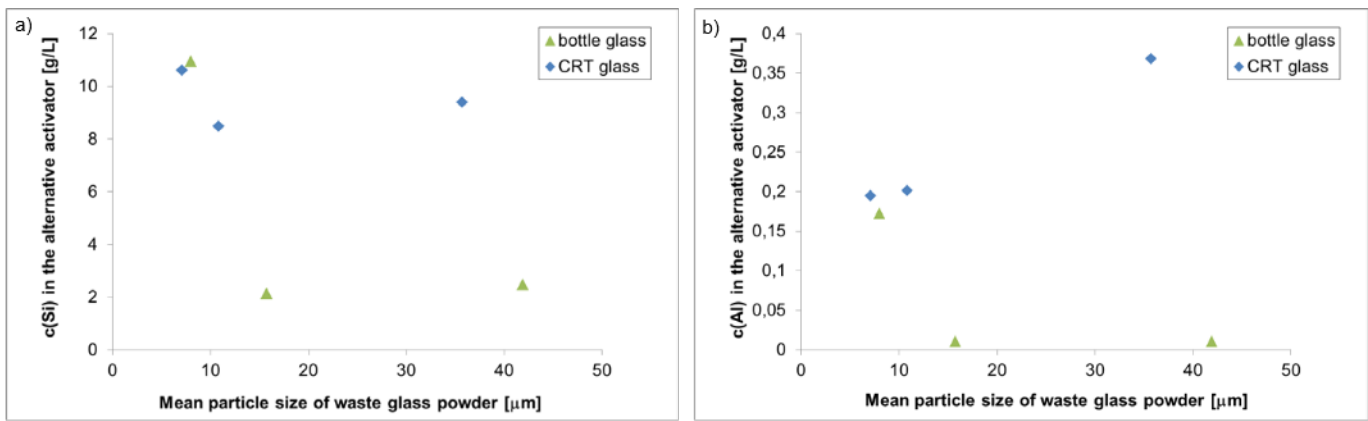


Figure 3: The concentration of a) silicon (c(Si)) and b) aluminium (c(Al)) as a function of mean particle size of glass powder (dissolution time 45 h)

With decreasing the particle size of bottle glass, silicon concentration in the alternative activator was increasing. When the largest particles (sieved through 90 μm- and 63 μm-sieve) were used, the silicon concentration in the alternative activator was only 2.47 g/L and 2.12 g/L, respectively. When larger particles were used, aluminium concentration in the alternative activator was very low, less than 10 mg/L. The waste bottle glass has a higher amount of silicon and less aluminium than cathode-ray tube glass. Due to higher aluminium content in the CRTG powder, a higher aluminium concentration in the activator was expected, but this was true only when a short dissolution time was used. The solubility of amorphous silica in aqueous systems increases strongly with pH and also with temperature. However, no data of solubility limit values of silicon in sodium hydroxide solutions at temperatures above 100 °C and pH above 13 exist to the authors' knowledge. Furthermore, in the scientific literature, the predicted solubility of total dissolved silica in NaOH solutions at very high pH differ by orders of magnitude, and the dissolution process is still not well understood [15]. The solubility values of amorphous silica and aluminium were predominantly reported for pure systems, where no additional ions were present in the solution. However, the dissolution of glass involves also other glass components that are released in solution and can influence the solubility limit of silicon and aluminium [16]. Due to described complexity, we report in our paper only a comparison to the concentrations of silicon in alternative activators obtained in some other published works where similar dissolution processes of waste glasses were applied [9, 17]. The obtained concentration of silicon in the BG activator (17 g/L after 24 h of dissolution) agrees well with previous research performed by Puertas et al. [18]. The concentration of SiO₂ in an alternative activator prepared from waste glass powder of particle size 45 μm in NaOH/Na₂CO₃ solution (0.1 g/mL), heated for 6 hours at 85 °C, was 2.83 g/100 mL (13.16 g Si/L).

3.2 The properties of hardened binders

The alternative activators were mixed with fly ash, cured at 70°C for 72 h, and then the mechanical strength of the hardened binders was determined. The calculated molar Na/Al/Si ratios, mass ratios of liquid to solid (L/S) in the prepared pastes, and the density, compressive and bending strength of the hardened binders are summarised in Table 3.

Table 2: The calculated molar Na/Al/Si ratios, the mass ratio of liquid to solid (L/S) in the prepared pastes and the density, compressive and bending strength of the corresponding hardened binders

Specimen	The molar ratio of Na/Al/Si in the prepared mixtures	The mass ratio of liquid to solid (L/S) [l]	Density [g/cm ³]	Compressive strength [MPa]	Bending strength [MPa]
73.2FA24.4NS2.4NaOH(s)	0.9/1/2.0	0.32	1.91	70.43	10.13
80FA8.8NS11.2BGA-24h	0.9/1/1.7	0.25	1.85	41.78	7.23
80FA8.8NS11.2CRTGA-24h	0.9/1/1.7	0.25	1.85	40.13	8.05
80FA8.8NS11.2NaOH(aq)	0.8/1/1.6	0.25	1.82	40.5	7.8
77FA23BGA-24h	0.4/1/1.4	0.30	1.67	31.31	7.39
77F23CRTGA-24h	0.4/1/1.4	0.30	1.67	33.00	8.16
77F23NaOH(aq)	0.4/1/1.4	0.30	1.67	38.98	9.16

Figure 4 shows a) the compressive and b) bending strength of hardened fly ash pastes synthesised from alternative activators. A reference sample prepared with 73.2 % of fly ash, 24.4 % of commercial sodium silicate, and 2.4 % of NaOH flakes had the highest compressive strength (70 MPa) and the highest bending strength (10 MPa). When the paste contained 80 % of fly ash, 8.8 % of commercial sodium silicate, and 11.2 % of BG activator ($c(\text{Si}) = 17 \text{ g/L}$), CRTG activator ($c(\text{Si}) = 15 \text{ g/L}$) or 10 M NaOH, the compressive strength decreased to 40 MPa and bending strength was between 7 MPa and 8 MPa. When the paste contained 77 % of fly ash and 23 % of BG activator or CRTG activator, the compressive strength was 31 MPa and 33 MPa, respectively. The hardened paste produced from 77 % of fly ash and 23 % of 10 M NaOH had a compressive strength of 39 MPa.

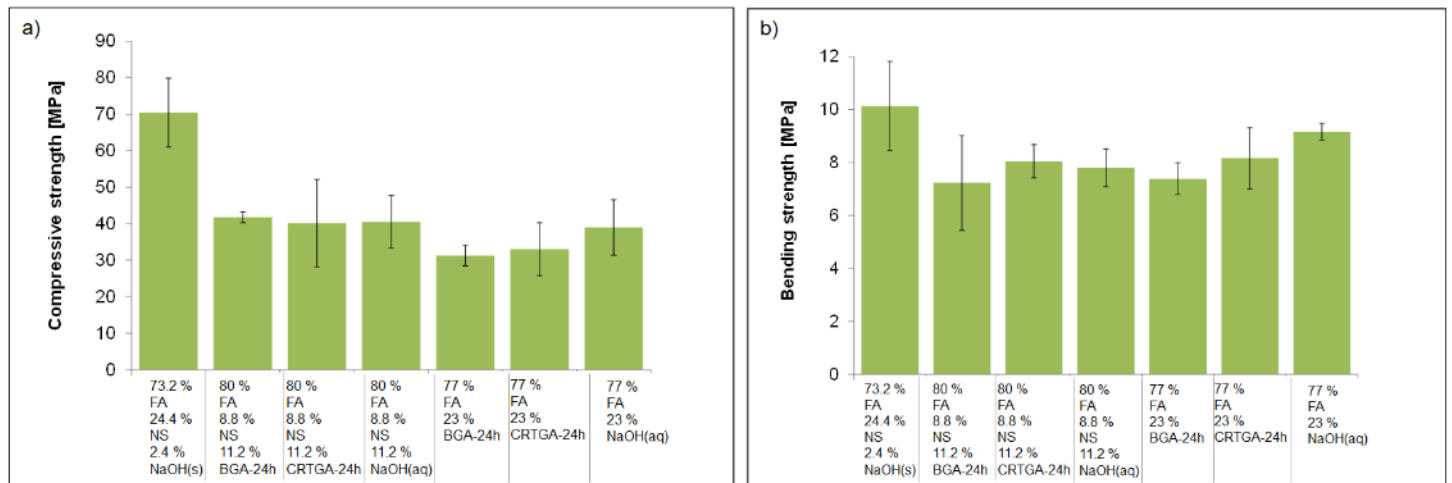


Figure 4: Compressive strength (a) and bending strength (b) of the hardened binders prepared by alkali-activation of fly ash using BG and CRTG alternative activators and commercial water glass or 10 M NaOH, after curing at 70 °C for 72 hours

The mechanical strength measurements indicate that only simultaneous addition of commercial sodium silicate and solid sodium hydroxide resulted in excellent mechanical properties of the hardened binders. Conversely, the alternative BG and CRTG activators presented less sufficient binding of the fly ash particles. Furthermore, fly ash contains a high amount of amorphous silicon, and for this reason, it is feasible to prepare hardened binders with good mechanical strength only by mixing fly ash with concentrated sodium hydroxide. Further research effort should be devoted to using other precursors with less available amorphous silicon and synthesising alternative activators with higher silicon concentration.

Figure 5a shows the micrograph of the hardened specimen composed of fly ash and an alternative BG activator. As in our previous investigation [19], also in this study, a similar pattern was observed in all the investigated specimens. Therefore, only one representative micrograph with the corresponding chemical composition of the AAM gel determined by EDS analysis is presented (Figure 5). A major part of the surface is composed of AAM gel; however, there are also many unreacted fly-ash particles. These particles differ in their diameter (ranging between 1 μm and 100 μm), are spherically shaped and are present in all samples regardless of the activator used. In addition to the prevailing presence of oxygen, the EDS analysis of the AAM matrix also revealed silicon, aluminium and sodium in the comparable molar ratios ($\text{Na}/\text{Al}/\text{Si}$) as already calculated based on the XRF measurements (Table 3).

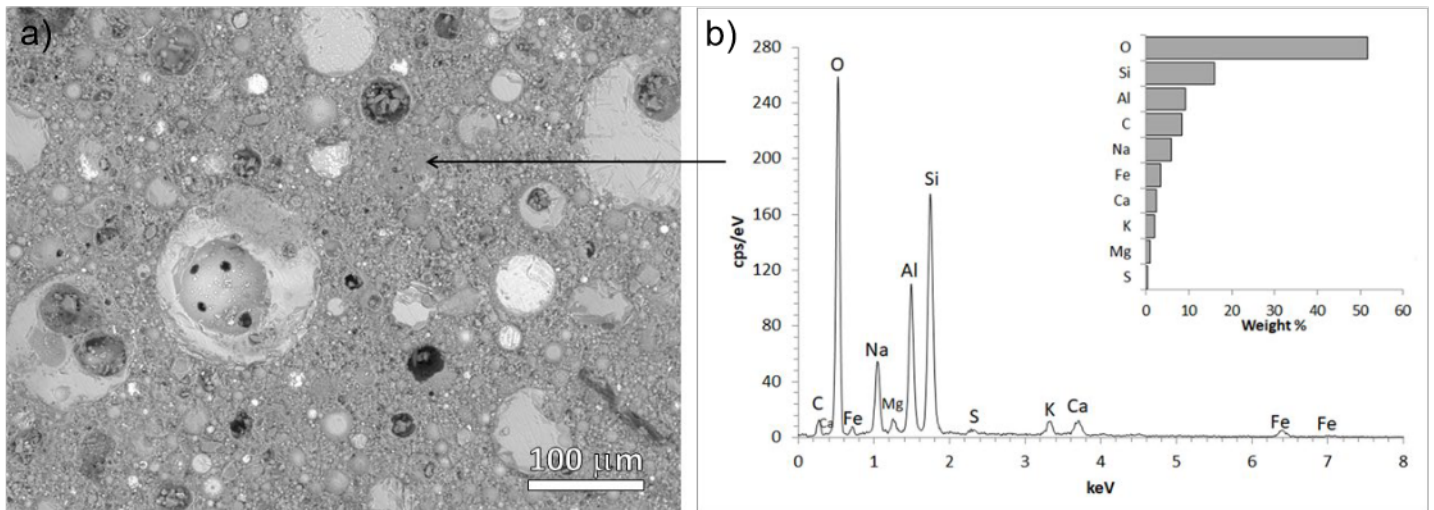


Figure 5: a) SEM micrograph of the hardened specimen composed of 77% fly ash and 23 % alternative bottle glass activator and b) EDS spectrum of the gel formed during alkali activation

4 CONCLUSIONS

Alternative alkali activators were prepared by treating waste bottle glass and cathode-ray tube glass in boiling 10 M NaOH solution. With increasing dissolution time of bottle glass and CRT glass in 10 M NaOH from 4 hours to 24 hours, the silicon concentration increased. However, when dissolution time was further increased to 45 hours, the concentration of silicon decreased. The highest achieved concentration of silicon in the filtrates was up to 19 g/L. The obtained filtrates were applied in alkali activation of fly ash, and the mechanical properties of hardened binders were determined. The addition of 24.4 % of commercial sodium silicate and 2.4 % of solid sodium hydroxide to fly ash yielded a hardened binder with compressive strength of 70.4 MPa after thermal curing at 70 °C for 72h. When 56 % of commercial sodium silicate was replaced with alternative activators sourced from bottle glass and CRT glass in the fly-ash mixtures, the compressive strength of hardened binders decreased to 41.8 MPa and 40.1 MPa, respectively. The addition of 23 % of 10 M sodium hydroxide to the fly ash mixture yielded a hardened binder with a compressive strength of 39.0 MPa, so silicon in the amorphous phase of fly ash was dissolved, and aluminosilicate hydrate gel with relatively good binding properties was formed. The reaction of fly ash with 23 % of alternative activators sourced from bottle glass and CRT glass yielded hardened binder with compressive strength of 31.3 MPa and 33.0 MPa, respectively. The results of mechanical strength measurements of the hardened binders indicate that the concentration of silicon obtained in the hydrothermal process is still too low to produce hardened binders with performance similar to that of hardened binders based on the commercial sodium silicate.

ACKNOWLEDGMENTS

We acknowledge financial support from the Slovenian Research Agency, Slovenia, through project No. J2-9197: Synthesis and characterisation of alkali-activated foams based on different waste.

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