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Development of geopolymer using industrial waste materials

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Abstract

Coal burned thermal power plants are producing large amounts of solid waste, fly ash. The disposal of this waste is a huge environmental problem at this moment. Generally, fly ash particles are very fine ($< 100 \mu\text{m}$) and mainly round shaped and glassy materials form an outer shell on it. According to several authors the attrition or grinding of this shell improves the activity of the fly ash. This paper deals with the laboratory investigation of ground fly ash based geopolymer. This material can be applied in many fields, mainly in the construction industry, e.g. non-structural elements, concrete, pavements and products, containment and immobilization of toxic, hazardous and radioactive wastes, advanced structural tooling and refractory ceramics, and fire resistant composites used in buildings, etc...

In this study, the main process engineering properties of the raw materials, such as particle size distribution, moisture content, density and specific surface area are shown. Beside fly ash, red mud in different rate was used to prepare geopolymer. Systematic experimental series were carried out in order to optimize the preparation process. The particle size distribution of fly ash was measured by laser diffraction, the structure of fly ash and geopolymer was determined by Fourier Transformed Infrared Spectroscopy (FT-IR). The strength of the formed geopolymers was characterized by the uniaxial compressive strength. Additionally, leaching tests were carried out to monitor the stability of the main element of the fly ash. The product properties were studied as function of fly ash fineness.

As a result of the investigation it was found that the geopolymer strength increased as function of fly ash fineness. Furthermore, it was established that the red mud had a positive effect on geopolymer strength. Therefore, the synergetic application of the above wastes is of good potential to create an industrial final product. Of course, several further experimental work is necessary to study the system from environmental point of view.

Keywords: fly ash; red mud; geopolymer; mechanical activation.

Nomenclature

$F(x)$	cumulative particle size distribution, PSD
n	moisture content (%)
S	specific surface area (cm^2/g)
t	grinding time (min)
x_{50}	median particle size (μm)
x_{80}	80% particle size (μm)
ρ_p	particle density (g/cm^3)
ρ_{spec}	density of test specimen (g/cm^3)

1. Introduction

Geopolymers are amorphous aluminosilicates which can be produced by the reaction between silica and aluminosilicate in alkaline medium (NaOH and/or KOH) at ambient or elevated (30–100 °C) temperature. Due to its simple, energy efficient and eco-friendly production method, excellent durability and good mechanical properties geopolymers can replace conventional materials from low tech application (building industry, waste immobilisation) to high tech industry (ceramics with special properties, composites). Every material is suitable for geopolymer production which contains silica and alumina bearing phases, like primary (for example metakaolin) or secondary (fly ash, steel slag, red mud, etc) raw materials [1].

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Fly ash is a potential raw material for geopolymers, thanks to the presence of SiO_2 and Al_2O_3 as the main components [2]. Limiting factor which obstructs the use of fly ash for geopolymerisation it is low reactivity. The reactivity of fly ash depends on its particle size distribution and the amount and composition of glassy phase [3–7]. Low reactivity of fly ash results in slow binding and early strength development. Many times the dissolution of fly ash did not finish before the final hardened structure was formed [3–7]. It has been proven that calcined materials like granulated blast furnace slag, fly ash and metakaolin (which are mainly amorphous) has higher reactivity during geopolymerisation reaction unlike uncalcined materials [1]. It can be explained that calcination activates materials from crystalline to amorphous structure and extra energy stored in them [1].

Somna *et al.* [8] studied NaOH-activated ground fly ash geopolymers, cured at room temperature. Ground fly ash with a median particle size of $10.5\ \mu\text{m}$, was used as raw material mixed with NaOH as an alkali activator. Results indicated that ground fly ash gave higher strength geopolymer paste compared to original fly ash. The compressive strengths at 28 days of 20.0–23.0 MPa were obtained.

Paul *et al.* [9] carried out high energy ball milling of class F fly ash in order to convert it into nanostructured material. They found that the surface of the produced nano size fly ash has become more active as it was observed from FTIR studies. Morphological studies revealed that the surface of the nano structured fly ash is more uneven and rough and shape is irregular, as compared to fresh fly ash which are mostly spherical in shape. They achieved significant reduction in crystallinity in high energy milled fly ash after 60 hours residence time.

Fu *et al.* [10] investigated the physical–chemical characteristics of mechanically-treated circulating fluidized bed combustion (CFBC) fly ash. The water requirement decreases with prolonged grinding time, and slightly increases during the last stage of grinding. The pH of ground CFBC fly ash is greater than that of the original CFBC fly ash, indicating that ground samples react more rapidly with water. The intensity of the crystalline phases of ground CFBC fly ash decreases, while the half peak width of ground CFBC fly ash increases with prolonged grinding time, which means that ground fly ash has a higher reactivity than the original fly ash.

Hounsi *et al.* [11] investigated the influence of mechanical activation of raw kaolin on the final compressive strength of as-obtained geopolymers. Mechanical activation was performed by dry ball-milling of raw kaolin at 250 rpm for 1 h. Mechanical activation was performed to improve mechanical properties. Results showed that without mechanical activation, the optimal curing condition was 24 h at $70\ ^\circ\text{C}$ and the compressive strength was 15 MPa after 28 days of ageing. Under mechanical activation, improvement of the compressive strength was obtained with a curing time of 72 h at $70\ ^\circ\text{C}$ (35% increase) or with a curing temperature of $100\ ^\circ\text{C}$ (76% improvement). The formation of alkaline aluminosilicate gels and new crystalline hydrated phases controlled the strength development of geopolymers while the occurrence of carbonated species was responsible for the degradation of mechanical properties.

Kumar and Kumar [12] investigated red mud, a residue of Bayer's process to be used synergistically with fly ash to develop geopolymer. An improvement in intensity of reaction was observed with the red mud addition at all replacement level but improvement in setting time and compressive strength was observed only in the samples containing 5–20% red mud. Structural characterization revealed that rate of reaction was dependent on the NaOH concentration but the development of mechanical properties were related to the compact microstructure which was developed due to the combined effect of NaOH concentration, solubility of silicates and the presence of iron oxides. Based on scientific understanding, paving blocks using 10% and 20% red mud was developed.

Van Riessen *et al.* [13] examined various industrial residues to manufacture geopolymers, these relatively new cements have the ability to bind a range of contaminants. As the Bayer process could achieve significant process impurity removal by utilisation of plant liquor, synergy between the alumina and geopolymer industries could be achieved. Geopolymers with a Si/Al ratio of 2.3 and a Na/Al ratio of 0.8 were targeted. With only synthetic plant liquor as the alkali activator, geopolymers with a mean compressive strength of 33 MPa were synthesized, while use of processed plant liquor resulted in compressive strengths of 43 MPa.

The aim of the present research reported in this study primary is to study the effect of grinding on the structure of fly ash based geopolymer and to examine the relation between fly ash fineness and geopolymer compressive strength. Additional goal was to investigate the dependence of strength on the concentration of alkaline activator.

2. Materials and methods

The lignite fly ash sample used for laboratory experiments is originated from Mátra Power Station (Visonta) which mineralogical composition beside red mud (Almásfüzitő) sample can be found in Table 1. The mineral composition of the fly ash was determined by a Bruker D8 Advance XRD powder diffractometer (Cu-K α radiation, 40 kV, 40 mA) in Bragg-Brenant geometry (with detector side graphite monochromator). To decrease planar orientation sample bin rotated in sample plane. X-ray diffraction patterns were recorded in $2\text{--}70^\circ(2\theta)$ range. Sample crystalline phases are detected by Bruker DiffracPlus software package in its EVA module ICDD PDF-2 (2005) database is employed for search/matching of phases. Quantitative evaluation was made by Rietveld fitting method on TOPAS3 software using FPM based instrument convolution. Structural data originated from AMCSD database.

The alkaline activator used for the preparation of geopolymer was NaOH solution in different concentration (6, 8, 10, 12 and 14 M).

Table 1. Mineralogical composition of fly ash and red mud

Lignite fly ash		Red mud	
Mineral	[%]	Mineral	[%]
Quartz	20,34	Hematite	45,47
Maghemite	4,22	Calcite	7,93
Hematite	3,91	Kankrinite	35,48
Anhydrite	7,08	Lime	1,8
Albite	4,71	Gibbsite	9,32
Albite K0.16	5,58		
Lime	1,61		
Amorph	52,5		

The particle size distribution (PSD) and specific surface area (SSA) are of great importance from the point of view of reactivity. The particle size distribution of the raw and the ground materials was measured by HORIBA LA-950V2 laser diffraction particle size analyzer in wet mode using distilled water as dispersing media and sodium-pyrophosphate as dispersing agent applying the Mie-theory as evaluation method. The specific surface area (SSA) was calculated using PSD data by the laser size software. The particle size distribution of the initial raw materials can be seen in Figure 1. The red mud sample can be characterized with a much finer particle size distribution than the fly ash sample.

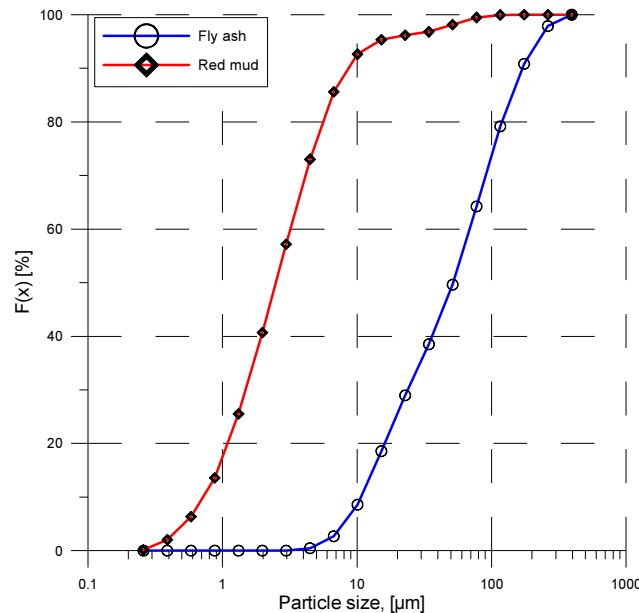


Fig. 1. Particle size distribution of fly ash and red mud samples

The particle density (ρ_p) was determined by pycnometer method using alcohol as media. Moisture content (n) of fly ash was very low 0.27%, however that of the red mud was significantly higher 33.64% measured in drying oven at 105 °C until constant mass. The drying time required to achieve constant mass varied depending on the type of the material. In most cases, an overnight (12–16 h) drying period is sufficient.

The structure of the fly ash and the geopolymer product was investigated by FT-IR. Stretching and bending vibrations of chemical bonds in samples induced by infra range electromagnetic waves detected by JASCO FT-IR 4200 type Fourier Transformed Infrared Spectrometer in reflection mode, a diamond ATR was used. Five tests were carried out parallel from each sample. One spectrum represents 32 FT-IR measurements with 4 cm^{-1} resolution number. The results are shown in Results and discussion Chapter.

The elemental analyses of the samples were carried out using ICP-OES followed alkaline ignition and dissolution by hydrochloric-acid.

3. Experimental

The mechanical activation experiments under dry condition were carried out in a conventional tumbling laboratory ball mill with the size of Ø303x305 mm internal diameter (smooth walled), with steel balls (max ball size 50 mm) as grinding media. The mill filling ratio of the grinding media was 30 V/V%, the material filling ratio was 110 V/V%. The operating revolution

number to critical revolution number (e) was 80%. Residence time of mechanical activation was 5, 10, 20, 30 and 60 minutes.

Geopolymer specimens made by mixing raw- or ground fly ash and NaOH solution using 0.67 liquid/solid ratio. Mixtures was placed to pre- oiled moulds and compacted by vibration. The compacted mixture was kept in moulds for 24 hours insulated at ambient temperature, before unsealed the specimens. It is followed by heat curing at 90 °C for 6 hours. After heat curing left the specimens cooled down to ambient temperature. The mechanical test was carried out by Compression Testing Machine in the age of 7 days.

Leaching tests were performed by distilled water and different strength acidic solutions (1 mol/l acetic-acid, 1 mol/l nitric-acid).

4. Results and discussion

4.1. Mechanical activation of fly ash

Mechanical activation through ultrafine milling is an effective procedure where an improvement in technological processes can be attained via a combination of several bulk and surface effects, which influence the properties of applied minerals [14, 15]. The primary effect of mechanical activation by grinding in our case was the particle size decrease and specific surface area increase, which is summarized in Table 2. After 60 minutes grinding in a ball mill 11.6 μm median particle size was achieved from the initial value of 52.04 μm , indicating a 4.49 size reduction rate. Additionally, the “outer” specific surface area increase was significant; from 1152.07 cm^2/g it reached 5425.55 cm^2/g due to ball milling.

Table 2. Characteristic particle size values and specific surface area of raw and ground fly ash

Characteristic particle size	Raw fly ash	5 min ground fly ash	10 min ground fly ash	20 min ground fly ash	30 min ground fly ash	60 min ground fly ash
x_{50} (μm)	52.04	43.82	29.84	21.29	18.94	11.6
x_{80} (μm)	119.32	91.72	69.67	49.09	43.58	27.9
Specific surface area (cm^2/g)	1152.07	1219.3	1500.29	1738.43	1928.9	5425.55

The variation of particle density (ρ_p) of the raw and ground fly ash can be found in Figure 2. Significant increase in the particle density was observed as function of grinding time. Namely, from the initial value of 1.94 g/cm^3 the density reaches 2.26 g/cm^3 after 20 minutes grinding time. It can be explained by the porous structure of fly ash.

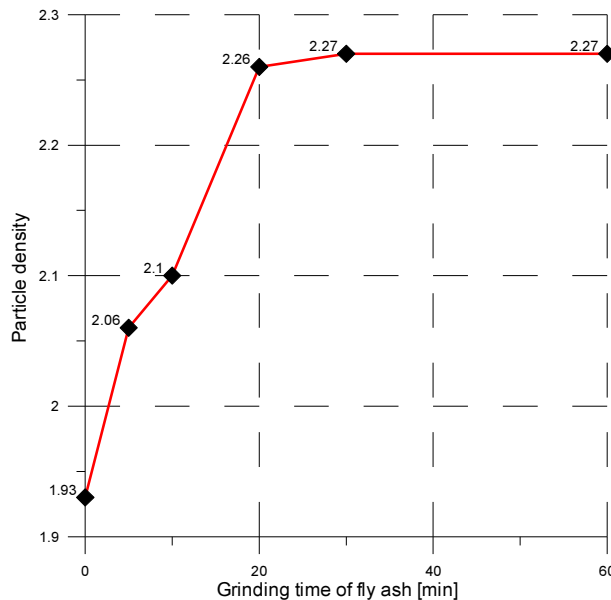


Fig. 2. Particle density as function of grinding time (t)

A plateau in the particle density-grinding time curve is reached after 20 min grinding time, after it only slight increase was detected in spite of that the material fineness is changed remarkably. It can be found that the material density of the investigated fly ash is 2.27 g/cm^3 .

4.2. Ground fly ash based geopolymer

The effect of grinding fineness on the geopolymer strength was carried out using 6 M concentration NaOH solution, the geopolymer paste was prepared from 40 m/m % alkaline activator (NaOH solution) and 60 m/m% mechanically activated fly ash. The density and uniaxial compressive strength of the geopolymer product was determined after 7 days of aging. These results can be found in Figure 3. Based on the specimen density (ρ_{spec}) values, it can be concluded that there is no difference between the 30 min and 60 min ground fly ash based geopolymer (1.35 g/cm³). This is in correlation with fly ash particle density results (Fig. 2). However, the compressive of the 60 min ground fly ash based geopolymer was 21.5% higher than that of the product consisting 30 min ground fly ash.

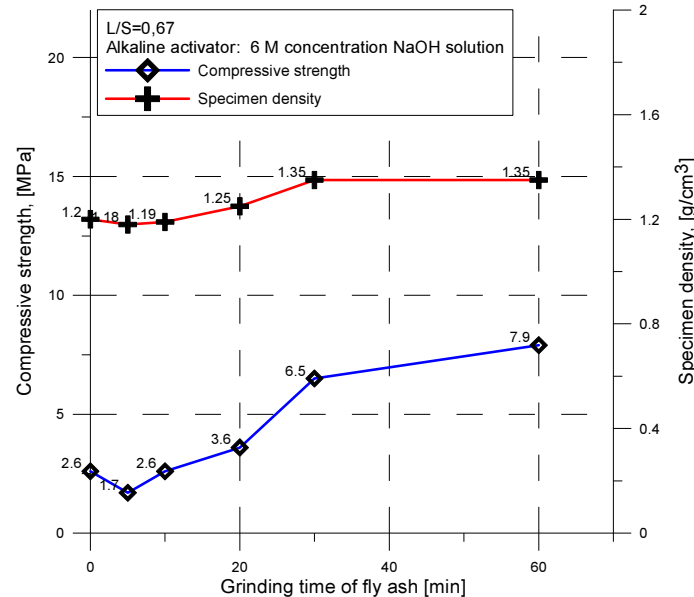


Fig. 3. Effect of grinding time of fly ash on the compressive strength and density of geopolymer test specimen

The highest geopolymer compressive strength was 7.9 MPa using 6 M NaOH solution as alkaline activator and 60 min ground fly ash.

4.3. The NaOH concentration

The optimal grinding time was determined previously which was found to be 60 minutes. Therefore this state of activation was used in the following experimental steps. The effect of concentration of sodium-hydroxide was examined using 6, 8, 10, 12 and 14 M solution, heat treated at 60 °C and 90 °C temperature.

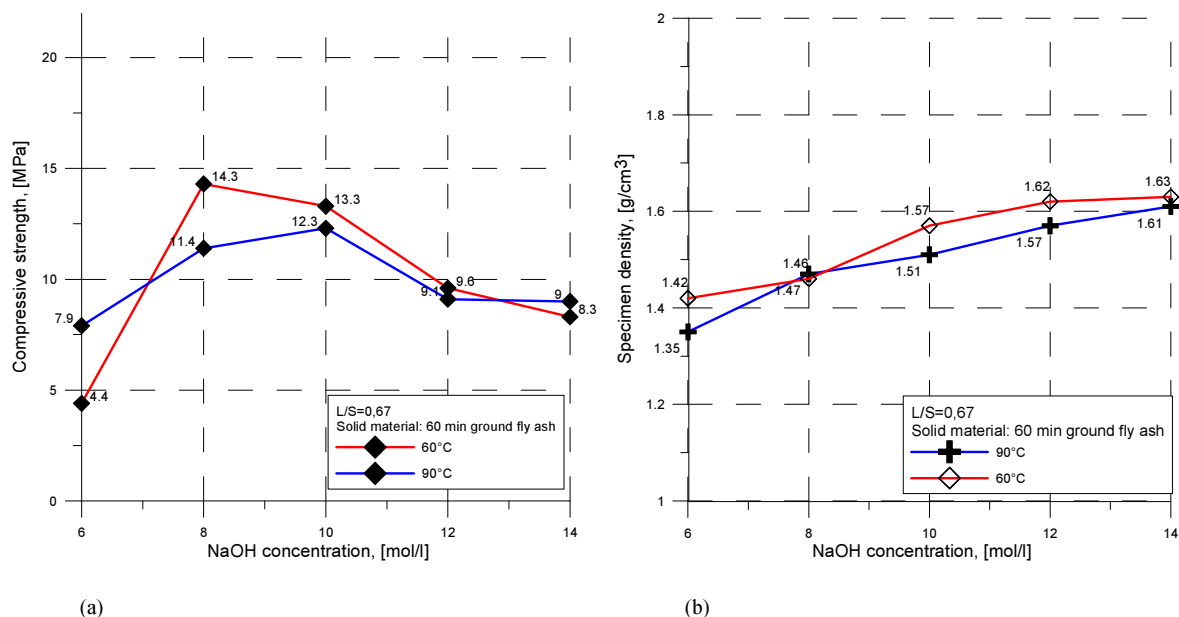


Fig. 4. Effect of NaOH concentration on geopolymer strength (a) and density of test specimen (b) using ground fly ash

From Figure 4 it can be observed that the highest compressive strength values was found using 8 and 10 M NaOH solution at both heat treated geopolymer. The most mechanical stable geopolymer was reached at 60 °C temperature using the 8 M concentration activator, which uniaxial compressive strength was 14.3 MPa. However, it is interesting that there is no correlation between compressive strength and density. Namely the density was only 1.46 g/cm³ in this case, after this point it reached 1.63 as a maximum but no strength increased was observed. To understand the phenomenon, structure of the geopolymer was investigated by FT-IR.

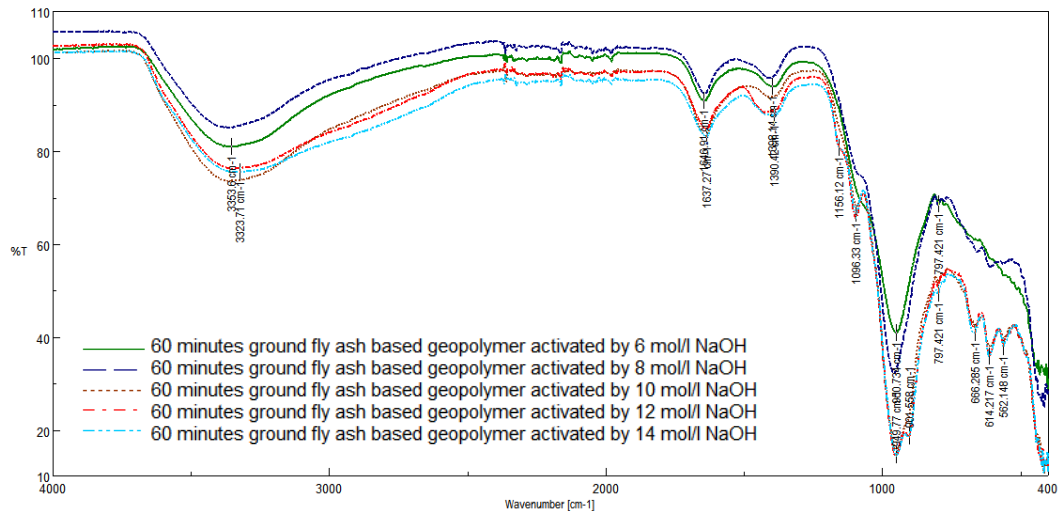


Fig. 5. FT-IR spectras of ground fly ash based geopolymer treated at 90 °C

The FTIR spectra of ground fly ash based geopolymer activated by different concentration NaOH solution can be seen in Figure 5. The peaks at 6 mol/l case corresponds to the presence of amorphous aluminosilicate gel (950 cm⁻¹, 797 cm⁻¹ assymetric and symmetric stretching vibraton of Si-O-Si and Al-O-Si bonds) and carbonate (1398 cm⁻¹, O-C-O stretching vibration). Peaks at 3350 cm⁻¹ and 1647 cm⁻¹ related to -OH, HOH stretching and bending vibration. By increasing NaOH solution concentration new peaks was observed; 1156 cm⁻¹ and 901 cm⁻¹ corresponds to assymmetric stretching vibration of Si-O-Si, Al-O-Si bonds, 797 cm⁻¹, 666 cm⁻¹, 614 cm⁻¹ and 562 cm⁻¹ related to symmetric stretching vibration of Si-O-Si and Al-O-Si. These differences prove that structural changes are between the geopolymers, which can give answer the cause of compressive strength decreasing. Probably, the formed geopolymer structure is not appropriate due to high Na⁺ presence, or the formed geopolymer structure partially dissolved in the high alkaline conditions.

4.4. Red mud additive

During the preparation of the geopolymer paste red mud was added in 5, 10, 15, 20, 25 and 30 % for the solid mass of fly ash. Alkaline activator NaOH with 6 M concentration was used in different ratio depending on the workability of the paste, namely for geopolymer paste containing 5% red mud the activator was added in 40 m/m %, for that of 10, 15 and 20%, the activator was added in 35 m/m %, finally for 25 and 30%, the NaOH solution was added in 30%.

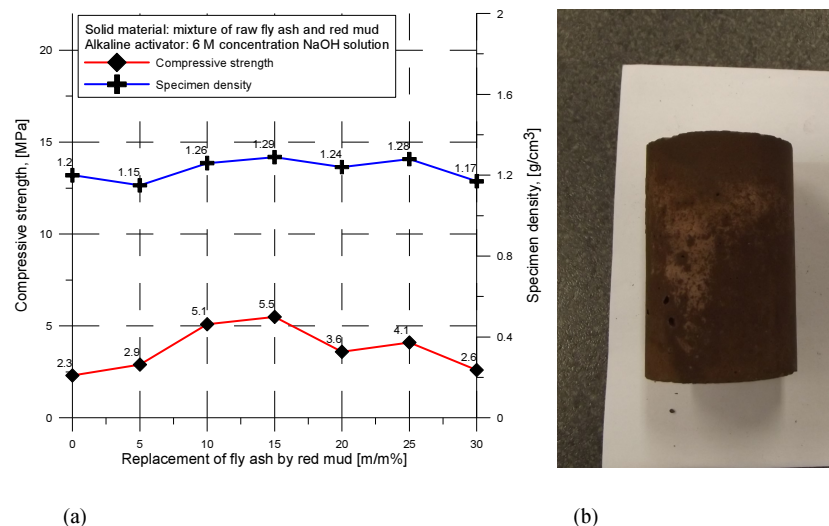


Fig. 6. a) Effect of red mud content on the geopolymer strength and density of specimen, b) Geopolymer specimens containing red mud (80% fly ash and 20% red mud)

The results of experiments can be found in Figure 6. Regarding the density values of geopolymer product the values are fluctuating in the range of 1.15 and 1.29 g/cm³. However, the strength values have a maximum point at 15 m/m % red mud content, which was 5.5 MPa.

The geopolymer test specimens containing 20% red mud beside 80% fly ash can be seen in Figure 6b. It can be observed that the characteristic red color of red mud will be dominant in the final product. It might be an advantage if commercialized product will be manufactured.

4.5. Leaching of main element of fly ash

The raw and mechanically activated (for 5, 10, 20, 30 and 60 min) fly ash was treated in 1, 5 and 10 M NaOH solution. After the phase separation the elemental content was determined of the solution phase. Based on the Figure 7 two main conclusions can be drawn: the effect of grinding can be seen clearly. The quantity of alkaline soluble silica and aluminium is increasing as function of grinding time.

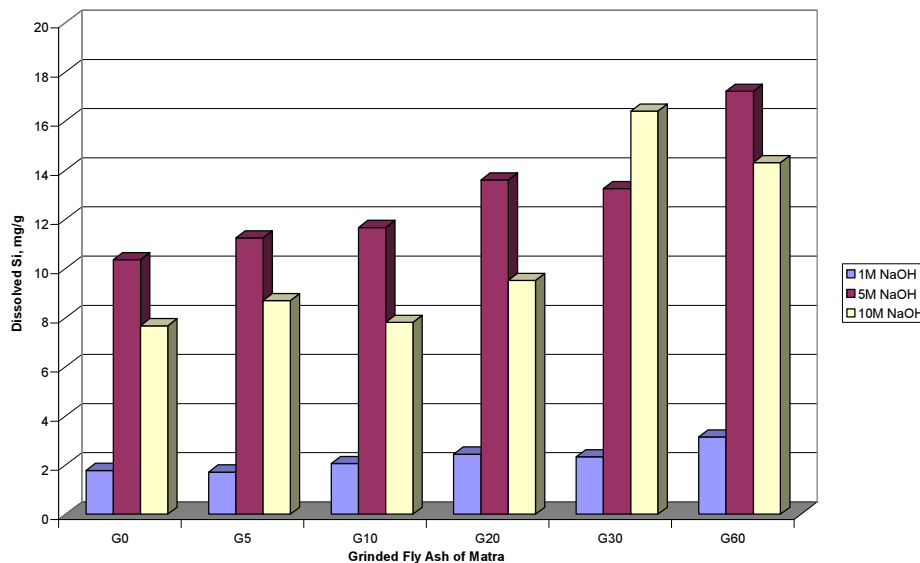


Fig. 7. Leaching of Si from mechanically activated fly ash (G0 – raw fly ash, G60 – 60 min grinding) at different concentration NaOH solution (1, 5 and 10 M)

The second observation is that as function of alkaline concentration, the quantity of leached silica and aluminium is increasing only until a certain alkaline concentration, after that point it drops down (see 10 M NaOH results).

5. Conclusions

Based on the experimental results presented above the following conclusions can be drawn:

- The mechanical activation by ball mill caused significant increase in material fineness (5425.55 cm²/g) and in particle density of the fly ash investigated.
- The grinding fineness improved the geopolymer uniaxial compressive strength from the initial 2.6 MPa up to 7.9 MPa.
- The optimum NaOH concentration of the alkaline activator was 8 M for 60 °C heat treatment (maximum compressive strength was 14.3 MPa) and 10 M for 90 °C.
- FT-IR spectras shows structural differences between ground fly ash based geopolymer activated by different concentrated NaOH solution. The cause of compressive strength decreasing is persumably that the formed geopolymer structure is not appropriate due to high Na⁺ presence, or the formed geopolymer structure partially dissolved in the high alkaline conditions.
- The addition of red mud in different portion tailored the compressive strength of the final product until a certain concentration (20 m/m %), after started to decrease. The maximum strength reached was 5.5 MPa.
- The quantity of alkaline soluble silica and aluminium of fly ash is increasing as function of grinding time.
- Further goal of the research is to carry out leaching test of toxic component of geopolymer and its raw materials.

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