



## STRUCTURAL FORMATION AND LEACHING BEHAVIOR OF MECHANICALLY ACTIVATED LIGNITE FLY ASH BASED GEOPOLYMER

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**Abstract.** Geopolymers are inorganic polymers which can be produced by the reaction of aluminium silicate oxides and alkaline silicates in an alkaline medium. Nowadays, silicate bearing wastes, such as fly ash or slag and other by-products of power stations are very common raw materials for geopolymers.

In our research a lignite type fly ash was mechanically activated in a high energy density mill (HEM) for different retention time, and geopolymer specimens were produced from these materials. After determining the optimal fly ash fineness, the concentration and composition of the alkaline activator solution were also investigated. The highest compressive strength was reached using fly ash with 2 m<sup>2</sup>/g specific surface area, activated with a mixture of Na-K silicate (water glass) and NaOH solution. The total dosage of alkaline activators to the fly ash was 40 m/m%, the NaOH activator of 12 M solution represented 25 m/m%, while Na-K silicate 75 m/m%. Then, the leaching properties of the main components and the mobility of toxic elements of the produced geopolymers were tested in distilled water, 1M acetic acid and 1M hydrochloric acid as well. The lowest mobility of the elements was obtained in most cases by the activator containing 100m/m% Na-K silicate solution (water glass) using the mechanically activated fly ash.

**Keywords:** fly ash, mechanical activation, geopolymer, leaching.

### Introduction

Coal firing power plants generate fly ash and slag in huge amount worldwide, about 780 million tons/year (Heidrich *et al.* 2013). Due to the relatively low utilization rate, enormous quantities of these wastes are landfilled in ponds. The fly ash is the finest grained particle fraction of the solid ash which is transported with flue gas, and removed by electrostatic or bag filters. The fly ash has pozzolanic properties and pozzolanic activity, the latter itself does not react with water, but in the presence of calcium hydroxide solution hardens and solidifies, producing a practically insoluble in water reaction product (Opoczky 2001). The most important property of the fly ash regarding geopolymerization is its reactivity, which depends on the chemical and phase composition, the dispersity (specific surface area, particle size distribution), and the morphology of the fly ash particles, and determined by the physical properties and chemical composition of the fly ash.

Geopolymers concerning their chemical structure are polysialates, where the sialate (silicon-oxo-aluminate) network is built up from the bonds of Si-oxide and Al-oxide by sharing oxygen atoms (Davidovits 1988).

The main disadvantage of the fly ash in production of geopolymers is its low reactivity. One way of improving its reactivity is the mechanical activation (MA). According to Pietersen *et al.* (1989) and Brouwers and van Eijk (2002), the inner surface of the fly ash is more active than the outer shell, therefore, not only a larger surface area is obtained during the mechanical activation, but the inner surface with higher reactivity is liberated and will be available for the reaction, so the geopolymerization can be more efficient and faster.

The geopolymerization contains the following steps according to Hardjito and Rangan (2005):

- dissolving the solid aluminium-, silicon oxides and silicates in the alkaline activator solution (MOH wherein M: alkali metal, Na or K);
- diffusion or transport of dissolved Si and Al complexes from the particle surface to the inter-particle reaction space;
- finally, the polymerization of dissolved particle parts and added silicate solution providing the hardening of silicate structure.

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Arioz *et al.* (2012) activated an F-type fly ash with 12M NaOH solution and water glass in their experiments. The specimens were cured at 40, 80 and 120 °C for 6, 15 and 24 hours residence time. The broken specimen at 28 days was ground and the sample was tested by leaching using ICP-OES for the leached element analysis. According to the US EPA 1311 method the pH of the acetic acid used as a solvent was set to  $4.93 \pm 0.05$  before the leaching test. The ratio of liquid-to-solid material was 20:1. After 18 hours contact time the slurry was filtered and the liquid phase was measured by ICP-OES. It was concluded, that the As and Hg could be immobilized in the structure, while the other examined metal ions (Zn, Cr, Pb and Cd) were not.

Cheng *et al.* (2012) examined the leaching of different heavy metals ( $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Cr^{3+}$  and  $Cd^{2+}$ ) from the geopolymers. The geopolymer was produced as a mixture of metakaolin and alkaline solution, and then it was crushed down to the prescribed grain size for the leaching tests. It was established that the above mentioned heavy metals can be all immobilized in the structure of the geopolymer.

Izquierdo *et al.* (2009) compared the solubility of elements in geopolymer and in raw fly ash. They found that the fly ash based geopolymer is suitable for the immobilization of many trace elements, such as Be, Bi, Cd, Co, Cr, Cu, Nb, Ni, Pb, Sn, Th, U, Y, Zr and the rare earth elements. However, the leached amount of some elements was higher in geopolymers in aqueous solution as compared with raw fly ash. As the effect of strong alkaline condition after geopolymerisation caused by the unreacted alkali content, the elements due to their mobility can form As, B, Mo, Se, V, W oxianions. Their concentration was found to be increased. This means that the ash composition, an optimal composition of the activator solution, the ratio of activator solution and the circumstances of production are very important in order to achieve a stable final product exhibiting a low mobility of the elements.

It is well known that the elements mobility can depend on its oxidation state. According to Füleky (2011) the toxic lead in the water and in the soil normally can be found in the form of  $Pb^{2+}$  ions. In the case of oxidizing circumstances it can turn into insoluble Pb (IV)-oxide. It can occur as adsorbed layer on the surface of tiny particles or in hydroxide or basic carbonate form as a precipitated material due to its small ionic radius and cation adsorption capacity of soils. Therefore, the adsorbable amount of Pb by plants is low. Although Bokányi *et al.* (2011) experienced the outstanding sequestering capacity towards lead by many micro- and macro algae biosorbents. Its mobility is negligible in weak acidic circumstances. The opposite can be found in case of Cr(III)-Cr(VI) system where the higher oxidation state form is the mobile one (Lakatos 2006).

Palacios and Palomo (2004) and Palomo and Palacios (2003) studied the immobilization of lead in fly ash based

geopolymer systems activated by sodium-hydroxide. It was established that the main reason of the effective encapsulation of lead is the formation of insoluble  $Pb_3SiO_5$ . The immobilization was more efficient if the activation state of the fly ash was higher.

According to Fernández-Jiménez *et al.* (2004, 2005) the As dissolution became higher in the case of geopolymer compared to the raw fly ash. Furthermore, authors stated that As occurs in Fe-rich regions of fly ash, which is in agreement with the previous observations, which claimed that arsenic could adsorb on the surface of Fe-hydroxide.

Chromium is in aqueous phase or as adsorbed on the surface of soil particles precipitated in the  $Cr^{3+}$  oxidation state. Only under highly acidic circumstances and in the presence of complex forming agents Cr(III) can become mobile. It cannot be leached by natural way from soil-groundwater system. Under strong oxidative circumstances chrome exists as Cr(VI) oxidation state, which is very toxic. In this form the chromium can be adsorbed on the surface of soil particles only in a small amount and could not precipitate, therefore the mobility of the Cr(VI) is much higher. Chromate ion is more oxidative under acidic circumstances, so easily oxidize organic materials, while the chromate transforms to Cr(III) state which is not toxic and has lower mobility, so it is more advantageous for the environment (Füleky 2011).

Deja (2002) examined the immobilization of Cr(VI) form in alkali activated slag based binders. It was concluded that in this structure the Cr(VI) is immobilized and the compressive strength of the product increased in case of carbonate and silicate activated systems. Reductive circumstances (by addition of free  $S^{2-}$  ions) effected positively the immobilization reaction due to the reduction of the Cr(VI) to Cr(III).

The fitoremediation of Cd is affected by the soil pH and the organic material content. Under acidic circumstances the adsorption of Cd in plants increased. In cadmium contaminated soils the lower pH resulted in the multiplying of Cd concentration in plants. Under alkaline or almost neutral conditions Cd can be adsorbed on soil particles, therefore with the addition of lime the absorption of Cd in plants will decrease. In case of high organic content the Cd mobility also decreases due to the low amount of the available Cd, since it has been fixed to the large organic molecules (e.g. humic materials) (Barati 2002).

Cadmium can be easily immobilized in Portland cement based binder materials due to the replacement of Ca, Ca/Cd forming silicate gel. Immobilization can also be achieved in alkaline silicate or carbonate activated slag systems, due to similar replacement mechanism (Deja 2002).

Zinc toxicity can appear only in acidic and organic material-rich soils in the case of high Zn concentration.

Sandy soils contain less mobile zinc, while solonetz soils contain more. The mobility of the zinc in the soil depends on the pH of the soil. Decreasing pH can result in the increase of the mobile zinc content (Barati 2002).

Copper is an essential element for the organisms of plants, animals and humans. Plants can extract copper from soil in Cu(II) ionic form. However, at higher concentration copper become toxic for living organism. Cu(II) ions exist in soil mainly in adsorbed state on soil particles or as precipitated hydroxide or basic carbonate form due to its relatively small ionic radius and high cation exchange capacity of soils. The mobility of the copper increases due to the acidification of the soils (Füleky 2011).

Temuujin *et al.* (2011) investigated the leachability of calcinated geopolymers. Calcination of the fly ash based geopolymers at 600°C resulted in a decrease of amorphous components from 63.4 to 61.6 wt.%. However, the solubility of the Al, Si and Fe ions in 14 M NaOH and 18% HCl after 5 days immersion decreased from 1.3 to 16-fold in comparison to as prepared geopolymer samples. Calcination of the geopolymer also resulted in a 30% reduction in compressive strength.

Several authors revealed that the mechanical activation of the geopolymer raw material (fly ash, granulated blast furnace slag) affected positively the properties of the final product (Kumar *et al.* 2007b; Temuujin *et al.* 2009; Mucsi *et al.* 2014).

Investigations of leachability show that mobility of a given element strongly depends on the structure which immobilizes it. Immobilization can be carried out in the structure with covalent bonds, or the fixed ions can be cohered only to dislocations or functional groups binding them by weaker forces. It is also important from the point of view of mobility of the fixed elements that the ionic forms of them are generated in accordance with the acid-base character of the leaching medium.

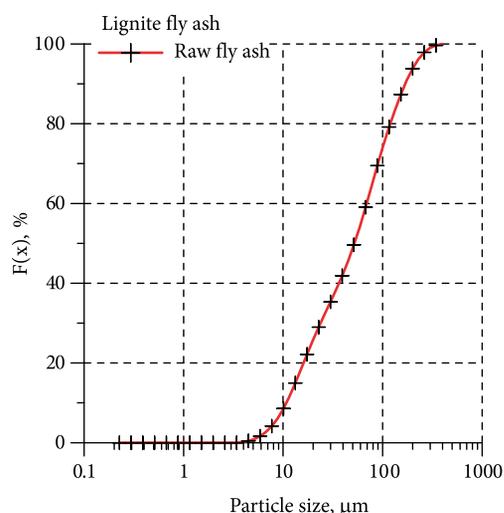


Fig. 1. Particle size distribution of the raw fly ash

Concerning the geopolymer production and application, the mobility of the main components of geopolymers (like Si, Al and Fe), as well as the toxic materials, is important.

The goal of the present work is to monitor the leaching characteristics of a mechanically activated fly ash based geopolymer under different conditions focusing on the main constituents and toxic elements. The main components mobility is essential concerning the network formation during geopolymerisation. Based on the toxic elements leaching the environmental compatibility of the obtained geopolymer could be evaluated. Further task of the research was to determine the optimal grinding fineness of the fly ash carried out by the mechanical activation from the point of view of compressive strength and specimen density.

## 1. Materials and methods

### 1.1. Materials

A lignite type fly ash was chosen for the investigation originated from Mátra Power Station, Visonta, Hungary. The determination of the particle density of the raw fly ash was carried out by pycnometer method in alcohol medium, the result of the raw fly ash was 1.88 kg/dm<sup>3</sup>. The initial moisture content of the fly ash was determined by drying at 105 °C in a drying cabinet until constant mass reached, resulted in 4.28%.

The particle size distribution was measured by Horiba LA 950 V2 type laser particle size analyzer and specific surface area was calculated from these data with shape factor 1.

Particle size distribution of the raw fly ash can be seen in Figure 1. Characteristic particle sizes and specific surface area of the raw fly ash are as follows:  $x_{50} = 52.04 \mu\text{m}$ ,  $x_{80} = 119.10 \mu\text{m}$ , SSA (cm<sup>2</sup>/g) = 1500 cm<sup>2</sup>/g.

In order to determine the chemical (oxidic) composition of the fly ash XRF analysis was carried out, the results are given in Table 1.

Main components presents in 95.2%, while other oxides in 4.8%. The SiO<sub>2</sub> content was relatively low 45.9%, while the Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> contents were average, the lime (CaO) content was higher than a typical in case of the F type fly ash. Additionally, the important SO<sub>3</sub> and L.O.I. content were 3.8% and 2.3% respectively.

The main mineral phases of fly ash are quartz, anhydrite and albite. The detailed quantitative phase composition of the fly ash can be seen in Table 2.

### 1.2. Methods

#### 1.2.1. Mechanical activation

The mechanical activation of the raw fly ash was carried out in a ceramic lined stirred media mill developed

Table 1. Chemical composition of the fly ash from (XRF analysis)

Main components	m/m%
SiO <sub>2</sub>	45.9
Al <sub>2</sub> O <sub>3</sub>	16.8
CaO	13.0
MgO	2.9
Na <sub>2</sub> O	0.50
K <sub>2</sub> O	1.8
Fe <sub>2</sub> O <sub>3</sub>	12.1
L.O.I.	2.3
Other oxides	
SO <sub>3</sub>	3.4
P <sub>2</sub> O <sub>5</sub>	0.28
TiO <sub>2</sub>	0.48
SrO	0.05
ZrO <sub>2</sub>	0.02
MnO	0.18
As <sub>2</sub> O <sub>3</sub>	0.03
CuO	0.02
ZnO	0.03

Table 2. Phase composition of raw fly ash

Mineral composition, m/m%	
Quartz	20.34
Maghemite	4.22
Hematite	3.91
Anhidrite	7.08
Albite	4.71
Albite K0.16	5.58
Lime	1.61
Amorphous	52.5

Table 3. Operating parameters of the stirred media mill

Parameter	Value
Diameter of the grinding balls mm	1.10–1.20
Diameter of the rotor disc, mm	153
Inner diameter of the grinding chamber, mm	174
Length of the grinding chamber, mm	250
Volume of the grinding chamber, dm <sup>3</sup>	4.00
Material density of the grinding balls, kg/m <sup>3</sup>	3591
Bulk density of the grinding balls, kg/m <sup>3</sup>	2160
Bulk volume of the grinding media, dm <sup>3</sup>	2.40
Porosity of the grinding media, %	39.80
Bulk density of the fly ash, kg/m <sup>3</sup>	850
Power of the motor, kW	5.50
Velocity of the rotor, m/s	5.00

by the Institute of Raw Material Preparation and Environmental Processing. The material of the liners and the seven stirrer discs were made of high wear resistant Al<sub>2</sub>O<sub>3</sub> ceramic. Grinding media was ceramic grinding beads with the diameter of 1.1–1.2 mm. Table 3 contains the main operating parameters of the mill.

The residence time of mechanical activation in the stirred media mill was 1, 3, 5, 7 and 10 minutes in dry state. Prior to the grinding the raw fly ash was dried in a drying cabinet during overnight to decrease moisture content.

#### 1.2.2. Particle size distribution

The particle size distribution and the calculated specific surface area (SSA) of the raw fly ash and its ground products were determined using a HORIBA LA-950V2 type laser particle size analyzer. From the measured data the computer calculated the particle size distribution according to the Mie-theory which takes into consideration the refractive index of the material. The measurement range of the analyzer is between 10 nm and 3 mm.

#### 1.2.3. Uniaxial compressive strength

The uniaxial compressive strength test was performed by a hydraulic strength testing machine (250 kN force).

#### 1.2.4. Fourier Transform Infrared Spectroscopy

The structural changes due to the geopolymerisation were detected by FT-IR method using a JASCO FT-IR 4200 type apparatus used in reflection mode equipped with diamond ATR type PRO470-H. Two spectra were made from each fly ash and geopolymer sample. Spectra are the average of 32 measurements with 4 cm<sup>-1</sup> wavenumber resolution.

#### 1.2.5. X-ray fluorescence

X-ray fluorescence measurements (XRF) were performed by a Rigaku Supermini 200 type XRF spectrometer. After determination of L.O.I. 1.00 g burned powder sample was mixed with 6.00 g lithium tetraborate (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>). The melted mixture was analyzed by fusion bead oxide method built in XRF software. L.O.I. values were taken into consideration. Every sample was analyzed three times then these values were averaged.

#### 1.2.6. X-ray diffraction

The mineral composition of the fly ash was determined by a Bruker D8 Advance XRD powder diffractometer (Cu-Kα radiation, 40kV, 40mA) in Bragg-Brentano geometry (with detector side graphite monochromator). X-ray diffraction patterns were recorded in 2–70°(2θ) 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.

### 1.2.7. Leaching tests

The aim of the leaching investigation was to determine the leachability of the main structural elements (Si, Al, Na) and the toxic components (Cr, Cu, Hg, etc.) under different pH values. Additionally the effect of retention time on leachability was studied. Since the geopolymer structure is changing for a relatively long time after its production, this change does not only effect the compressive strength, but also the immobilization properties. Therefore, two measurement series were carried out. The first series were tests after 10 days of polymerization, and the second one 4 months later. It is important to compare the results of the leaching tests with the prescribed concentration limits included in the Decree No. 20 of 2006 (IV. 5.) KvVM regarding the disposal of hazardous wastes in landfills. The experimental data from the leaching tests were compared with the prescribed concentration limit values related to the inert wastes.

It is important to note that the prescribed norm values are concerned to 10 L/kg liquid/solid ratio in distilled water as medium. However, in the case of the present investigation the liquid-to-solid ratio was 50:1 L/kg. The reason of this high ratio was to reduce the concentration of the acid consumer components (which remained in geopolymers from alkali activator solution) to keep the necessary acidity of the solution in order to dissolve the toxic components from geopolymers.

In the second measurement series both investigations were carried out using 10:1 and 50:1 liquid-to-solid ratio as well.

In both series distilled water, 1M acetic acid solution or 1M hydrochloric acid was used as leaching solution. However, in the case of geopolymers the distilled water extraction corresponds to a diluted alkali solution because of their remained alkali content. In the case of acids it corresponds to an extraction made by a system in which acid content was decreased by the quantity of the remaining alkali components.

The leachable element concentration from the raw material and from the formed geopolymers were determined by ICP-OES technique (Varian 720 ES horizontal torch). Multicomponent standard and the same matrix as the leaching solution were used for the calibration. The main component elements in the leachates were determined after an appropriate dilution with distilled water.

The leaching tests were performed on geopolymer particles in the size range of 1–2 mm. The contact time was five days.

### 1.3. Preparation of geopolymer

Two experimental series were performed in order to optimize the production circumstances of the geopolymer. The first one was carried out in order to determine the optimal fineness of the fly ash, the geopolymer specimens were prepared from fly ash activated in a stirred media mill for 1, 3, 5, 7 and 10 minutes residence time. Other optimal geopolymer production conditions, such as concentration of activator solution, compressing pressure, concentration of NaOH solution were determined previously.

During the second experimental series a certain part of the NaOH activator solution was replaced with water glass solution. Initially, Betol 39T (Na-silicate) then Betol SB (Na-K-silicate) type water glass was added to the mixture of the alkaline activator solution which consisted of 12M NaOH, as well as 12 M NaOH and water glass mixture. The water glass concentrations (replacement ratio of NaOH solution in the alkaline activator) varied in 25, 50, 75 and 100 m/m% in it.

During the preparation of geopolymer the first step was the mixing and homogenization of the alkaline activator solution and the mechanically activated fly ash. The geopolymer paste was mould into plastic moulds, followed by compression carried out in a TXM-V1-STC-07 consolidator with various pressures: 1.86, 3.73, 5.59, 7.46 and 9.33 bar. The residence time of the consolidation was 20 sec in each test.

The molded and compressed specimens were kept under sealed conditions and ambient temperature for 24 hours. Later the specimens were removed from the moulds and were heat cured at 90°C for 6 hours. Compressive strength tests were carried out at the age of 7 days. Chemical leaching tests were also carried out as written before.

## 2. Results and discussion

### 2.1. Mechanical activation

The variation of the specific surface area (SSA) of fly ash as function of specific grinding work can be seen in Figure 2. The different stages of the fine grinding process could be distinguished clearly. In the first, the so called Rittinger stage, until 3 min residence time, the increasing rate of the specific surface area was high. The relationship between specific grinding energy and specific surface area was linear. This was followed by the aggregation stage, between 3 and 7 min grinding time, where the specific surface area and surface energy become so high that particles could attach each other by van der Waals forces. The increasing rate then moderated, but specific surface area was still increasing during this stage. The final stage of fine grinding was the so called agglomeration stage, which started after 7 min residence time in our case, when particle surface

energy was even much higher, that particles agglomerated to each other by stronger bonds (for example, covalent ones). The most significant effect of this phenomenon is the coarsening of the particle size distribution. The maximum specific surface area reached after 7 min grinding time was 2.5 m<sup>2</sup>/g.

The compressive strength of the geopolymer specimens prepared from stirred media milled fly ash increased with the increasing fineness of fly ash until 3 min grinding time. After this stage the compressive strength values decreased (Fig. 3). The highest compressive strength was 4.14 MPa.

To detect the structural changes in the fly ash due to grinding FT-IR measurements were carried out (Fig. 4). The main peaks of the raw fly ash spectra were observed at 1100, 1020 (Assymmetric stretching vibration of T-O-Si T = Si/Al), 797, 675, 610 and 594 cm<sup>-1</sup> related to Si-O-Si symmetric stretching vibrations. Peak at 1455 cm<sup>-1</sup> related to stretching vibrations of O-C-O bonds which correspond to the presence of carbonate.

Structural changes were observed in the fly ash structure due to mechanical activation. The spectra show differences below 1500 cm<sup>-1</sup> wave number. The peak at 1100 cm<sup>-1</sup> detected in the case of raw fly ash disappeared after grinding even for 3 min residence time. Peak at 1020 cm<sup>-1</sup> shifted to 1036 cm<sup>-1</sup> (related to T-O-Si, where T = Si/Al asymmetric stretching vibration) in the ground products spectra. However, the peaks at 797, 676 and 593 cm<sup>-1</sup> did remain the same. The FT-IR spectra confirmed that structural changes took place due to the mechano-chemical effect of the grinding in stirred media mill.

**2.2. Effect of alkali activator on mechanical and structural properties of geopolymer**

During the laboratory investigations, beside NaOH, test specimens were prepared using two types of additives in the alkaline activator: Betol 39 T and Betol SB

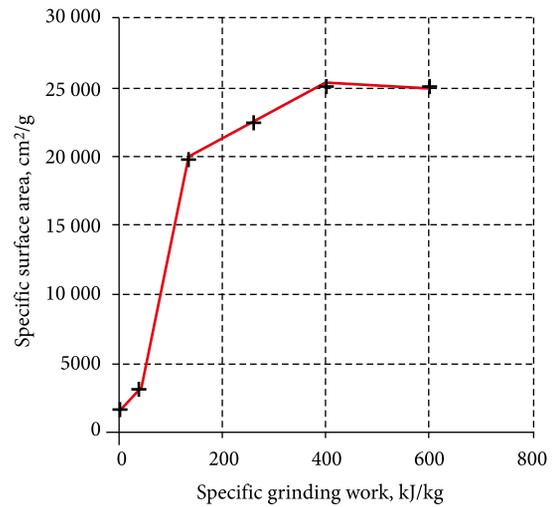


Fig. 2. Variation of specific surface area of fly ash as function of specific grinding work

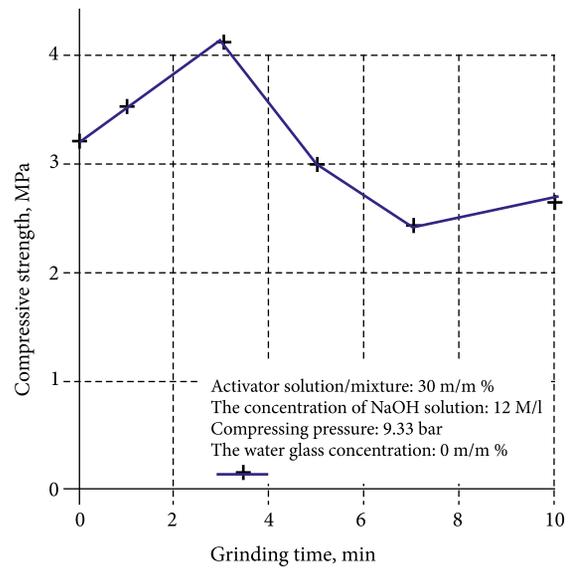


Fig. 3. Variation of compression strength as function of grinding time

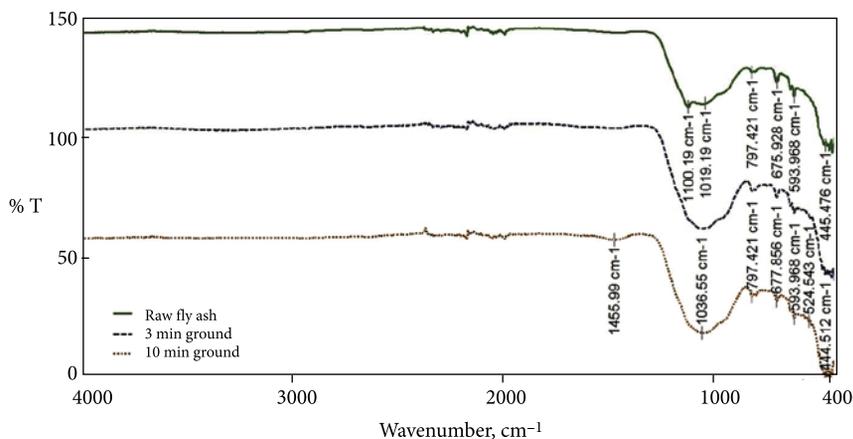


Fig. 4. FT-IR spectras of raw fly ash and mechanically activated fly ash for 3 and 10 min

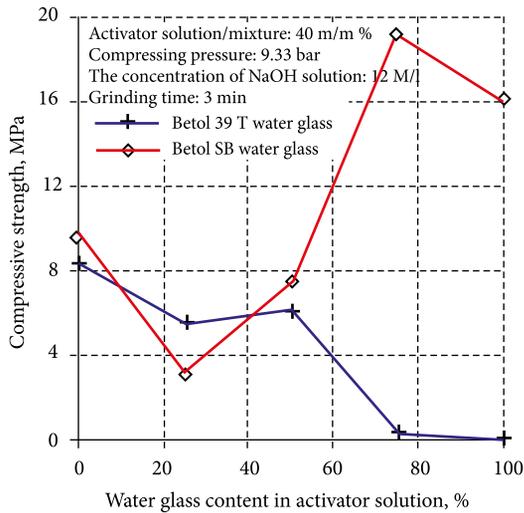


Fig. 5. Change of compression strength as function of water glass content in activator solution

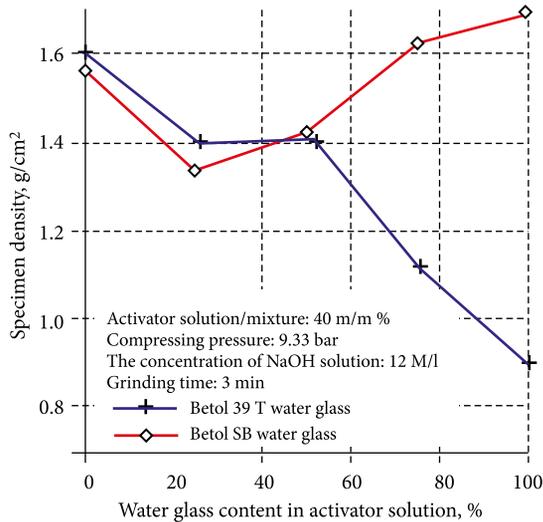


Fig. 6. Change of specimen density as function of water glass content in activator solution

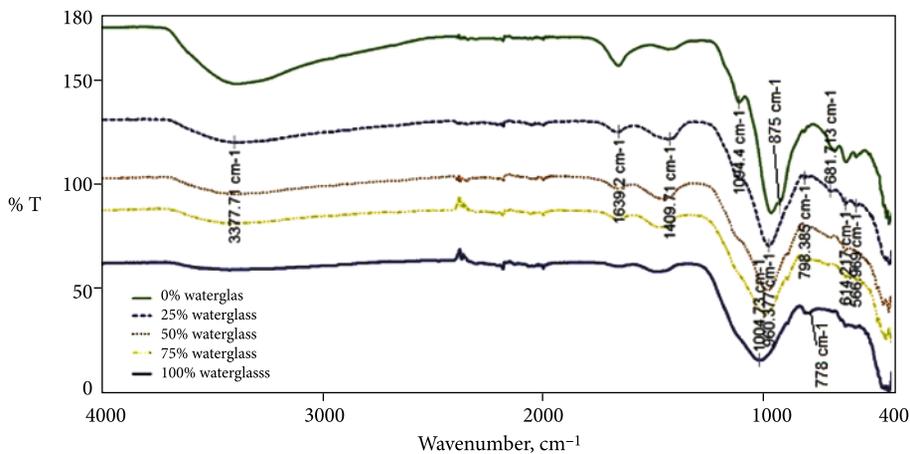


Fig. 7. FT-IR spectras of geopolymer prepared using water glass

(manufactured by Woellner, Austria) Na and Na-K water glass respectively. The optimal concentration of NaOH solution was determined in the previous stage of the systematic research (Research Report... 2014). It correlated well with the previous experience found in literature by other authors (i.e. Kumar *et al.* 2007a). They stated that by increasing NaOH concentration in activator solution the compressive strength of geopolymer increased. In the case of the Betol 39T water glass the fly ash particles conglomerated very fast, therefore workability of the paste reduced, a porous structure had been formed before an appropriate compaction.

The effect of different water glass types on the mechanical properties of geopolymer can be traced clearly in Figures 5 and 6. The compressive strength decreased significantly (except in case of 50 m/m % addition) when Betol 39 T was added to the alkaline activator solution (Fig. 5). The specimen density values were correlated well with the compressive strength (Fig. 6).

On the other hand, the Betol SB contains potassium in small amount beside sodium, which slows down the cross-linking of the molecules, therefore the workability of the geopolymer paste is better than that of the Betol 39 T in our case. The addition of Betol SB to the activator solution in 25 m/m% resulted in the decrease in compressive strength due to the not appropriate compaction, which fact is worth to be investigated later. However, further addition had a positive effect, the compressive strength increased dramatically up to 19 MPa, when Betol SB was added in 75m/m% as activator solution (Fig. 5). The highest specimen density value (1.69 kg/dm<sup>3</sup>) belongs to the case, when 100m/m% Betol SB was used as activator solution (Fig. 6).

The FT-IR spectra of the geopolymer are shown in Figure 7. The peak at 1409 cm<sup>-1</sup> appeared in the case of spectra belonging to the geopolymer produced without any addition of water glass (12 M NaOH only) and when

water glass (Betol SB) was added in 25 m/m% to the activator solution it shifted to  $1466\text{ cm}^{-1}$  (when only water glass was used). Peak (shoulder) at  $875\text{ cm}^{-1}$  disappeared when water glass was used, while at  $567\text{ cm}^{-1}$  (Si-O-Si and Al-O-Si symmetric stretching vibration) the addition of Betol SB resulted in a new peak. Spectrum corresponds to water glass addition in 25, 50 and 75 m/m % to activator solution shows minimal differences in the geopolymer structure. When only water glass was used peaks disappeared at  $682$  and  $566\text{ cm}^{-1}$ , others shifted to other positions (the peak at  $1409\text{ cm}^{-1}$  shifted to  $1466\text{ cm}^{-1}$ , peak at  $1093$  shifted to  $1004\text{ cm}^{-1}$ , and  $798$  to  $778\text{ cm}^{-1}$ ). The spectra presented in Figure 7 show structural differences between geopolymerisation performed using alkaline activator solution and the alkaline activator solution with water glass.

### 2.3. Leaching tests

#### 2.3.1. Leaching of the main elements (Si, Al, Ca, Fe)

A certain part of the alkaline activator added during the formation of geopolymers remains in a leachable form after the geopolymerisation, therefore the initially planned aqueous extraction would not be an aqueous one, but approximately 0.01M NaOH extraction. This explains the reason of the mobilization of main elements of geopolymer and fly ash, such as Si, Al and Ca. They are presented in the form of alkali soluble minerals in contrast with iron. Therefore, during the leaching tests of geopolymers the mobilization of only those elements can be expected, which do not form precipitates (Si) or they are soluble in the form of hydroxo-complex(Al) due to the alkaline pH of the aqueous extraction.

The retention time of geopolymerisation before the leaching tests was 10 and 120 days after the preparation of geopolymer specimen. For the latter tests the results of the leaching of the raw material (fly ash) were also given. This data can be used for the comparison of the alteration of the elements in the initial raw material and the obtained geopolymer. Unfortunately, this comparison is restricted, since in case of raw fly ash the leaching with distilled water differs from the leaching with distilled water in geopolymer case due to the above mentioned residual leachable alkaline.

As the leaching with distilled water in the raw material (fly ash) case shown in the Figure 8, only a small dissolution of the main components could be expected. The larger amount of Si achieved indicated that a part of the Si remained unused in the cross-linking process, or located on the weakly bounded position which was then mobilized by the weak alkaline leachate (distilled water = 0.01M NaOH). Higher mobilization of the Si could be expected only by the breaking the structure which could occur when the geopolymers were treated with acids. The

leached quantity of Si and other elements is demonstrated in Figures 8, 9 and 10.

The extraction results using distilled water represent only the quantities of the remaining Si which have not been built in the cross-linked network.

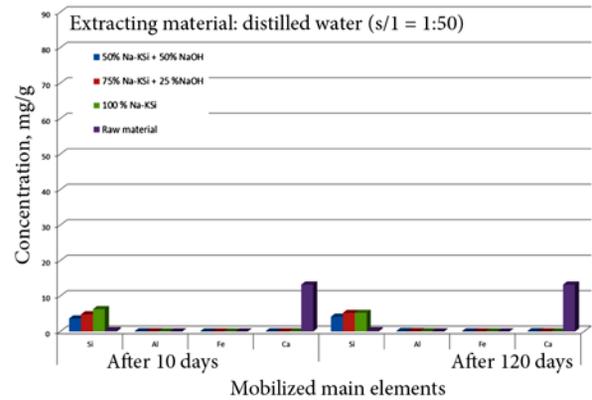


Fig. 8. Quantity of mobilized main elements in distilled water from 10 and 120 days age geopolymers formed using different alkaline activator solutions (solid/liquid ratio 1:50)

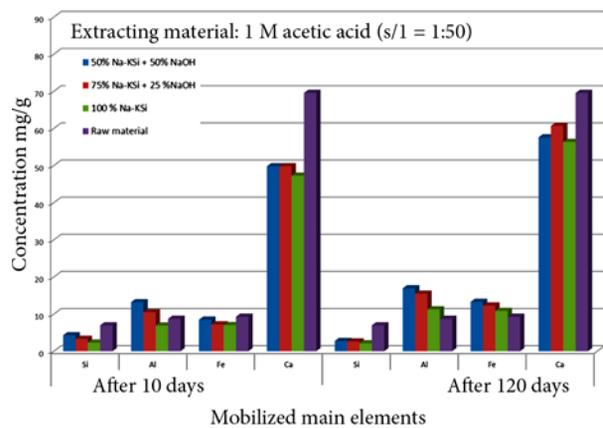


Fig. 9. Quantity of mobilized main elements from geopolymers (at 10 and 120 days age) using different alkaline activator solutions in 1 M acetic acid (solid/liquid ratio 1:50)

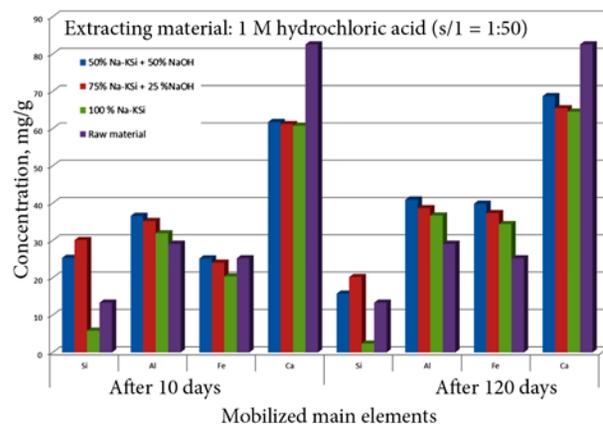


Fig. 10. Quantity of mobilized main elements from geopolymers (at 10 and 120 days age) using different alkaline activator solutions in 1 M hydrochloric acid (solid/liquid ratio 1:50)

In general, it can be observed that the increase of acidity results in a higher quantity of the soluble Si which originated from the decomposition of the structure.

The activator composition does have effect on the main component mobilization. The increasing the ratio of water glass results in a more stable and less leachable structure.

Using 1M acetic acid extracting solvent, significant acid excess can be found in the system. So that, beside the Ca-bearing minerals the cross-linked structure was attached and some Al and Fe was released (Fig. 9).

Regarding the examined elements the leached quantities shown slight decrease depending on the increase of the water glass content. The Al, Fe and Ca built in the structure in the largest proportion in the case of the geopolymer containing activator solutions Na-K silicate in 100%. Based on the above results of the 10 days geopolymer there are no significant differences regarding the different NaOH to water glass ratios based on the soluble components during the use of the 1 M acetic acid extracting solvent. However, after 4 months the soluble quantity of the examined elements was somewhat increased as compared to that of the 10 days age. This finding is contrary to the expectations, since a more stabilized structure with less soluble fraction is expected in case of longer polymerization time. If the difference is considered as the experimental uncertainty it can be stated that the leachability has not changed after the 10 days stabilization time.

The 1M hydrochloric acid as a strong acid dissolves the structure at a higher proportion than the 1M acetic acid. The mobility of Al and Fe increases as compared to the acetic acid extraction. The results of the leaching are represented in Figure 10.

The tendency of the leachability as a function of the water glass content was found being similar than that of the acetic acid leaching: the quantity of the leached components decreases.

### 2.3.2. Extraction of toxic elements

Regarding the environmental impacts of the geopolymer it is important to know the mobilizable toxic elements content. From this point of view, the comparison of the leached toxic element concentration to the limit values of the Decree No. 20 of 2006 (IV. 5.) KvVM will indicate the toxic or non toxic character of the geopolymers. According to the above Decree the aqueous extraction at L/S = 10 L/kg needs to be applied. It is important to note again that the soluble alkali remaining in the geopolymers turns the distilled water into a weak alkali solution, so the extraction with distilled water has to be interpreted as extraction with 0.01 M alkaline medium. Due to the presence of the alkali, minor mobility can be expected at those toxic elements which form hard-to-dissolve hydroxide precipitates. The dissolution of elements in the form of complex hydroxide may happen in this weak alkaline solution. The same situation can arise in case of oxo-anion forming elements. Regarding the measured data (see Fig. 11) the latter one can cause the environmental risk.

In the case of the examined toxic components it was found that the leached quantity of most of the elements remains under the limit values. However, arsenic, molybdenum and selenium exceeded the limit values concerning inert landfills determined in Decree No. 20 of 2006 (IV. 5.) KvVM. It can be explained as the effect mentioned above weak alkali media generated by the excess amount of alkali. Due to the unused alkali the appearance of elements

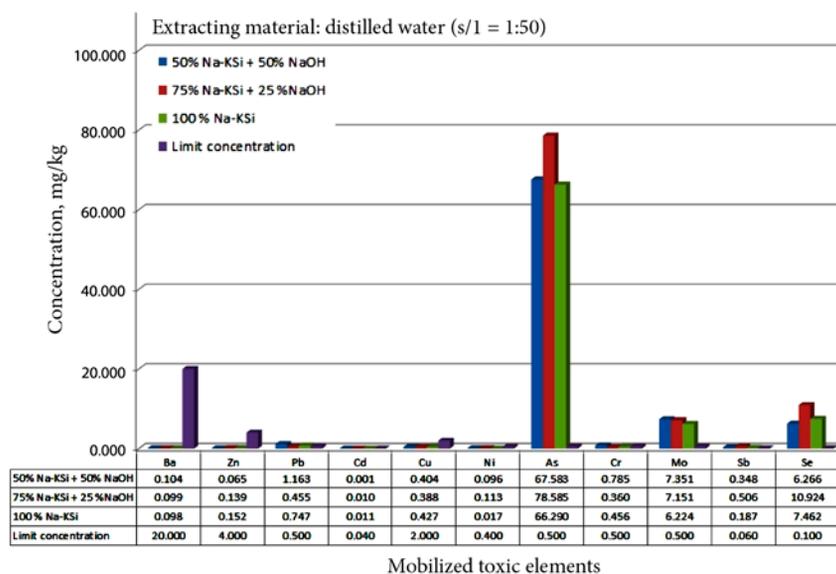


Fig. 11. Quantity of mobilized toxic elements from 10 days age geopolymers using distilled water as extracting material (solid/liquid ratio 1:50)

forming oxo-anions soluble in alkali (As, Mo, Se) can be expected.

According to the Decree No. 20 of 2006 (IV. 5.) KvVM, the limit value of leachable lead is 0.5 mg/kg. In our case the results (50% Na-KSi and 50% NaOH) show 1.16 mg/kg lead leaching, however, in the case of the geopolymer containing 75% water glass and 25% NaOH the quantity of the leached Pb decreased down to 0.45 mg/kg which is under the limit. The change in Pb mobility can be explained by the phenomenon of lead building-in to the geopolymer structure.

Palomo and Palacios (2003) and Palacios and Palomo (2004) established that the main reason of the effective encapsulation of lead is the forming of insoluble  $Pb_3SiO_5$  in fly ash based geopolymer systems activated with sodium-hydroxide.

The quantity of the leachable As significantly exceeds the limit concentrations concerning landfills (Fig. 11). It corresponds with the statement of Fernández-Jiménez *et al.* (2005). They found that the arsenic leaching from the geopolymers is higher than that of the raw fly ash.

During the second measurement, after 120 days the quantity of mobile As and Mo increases, the quantity of Se is almost the same as after 10 days ageing examination. Cd, Ni and Cr appears also, but Pb leaching could not be detected (Fig. 12).

The immobilization of Cd could correspond with the Ca-content of the geopolymer, because it substitutes the Ca. So the Ca/Cd silicate gel could form. According to Míneraková and Škvára (2006) in the low calcium-content geopolymers the immobilization of Cd does not always meet the strict environmental-protection regulations, and

often the rate of its leaching depends on the applied leaching standard.

Figure 13 represents the leaching results obtained in distilled water for 120 days ageing under 1:10 L/kg liquid-to-solid ratio as proclaimed in the Decree No. 20 of 2006 (IV. 5.) KvVM.

Regarding the examined toxic elements in the case of geopolymers we identified that the As, Mo and Se exceeded the limit concentrations, but the ratio of the exceeding is much lower than that obtained in case of 50 L/kg liquid-to-solid ratio. In the case of the geopolymer produced with activator solution containing 75% Na-KSi water glass and 25% NaOH the results of the examination concerning the case of 10 L/kg liquid-to-solid ratio are as follows. For As: 84.34; for Mo: 10.35 and for Se: 0.146 mg/kg. In the case of 50 L/kg liquid-to-solid ratio these values were 100.81; 20.377 and 1.55 mg/kg respectively. It means that the dissolution depends on the solid-to-liquid ratio as well.

**Conclusions**

Based on the results obtained in course of the experimental research work the following conclusions can be drawn:

- Mechanical activation of the fly ash improves the geopolymer compressive strength until a certain fineness (2 m<sup>2</sup>/g). During the further grinding the compressive strength of geopolymer decreases.
- The addition of the potassium type water glass to the NaOH activator solution significantly improves the workability of the paste and makes possible to tailor the mechanical stability.

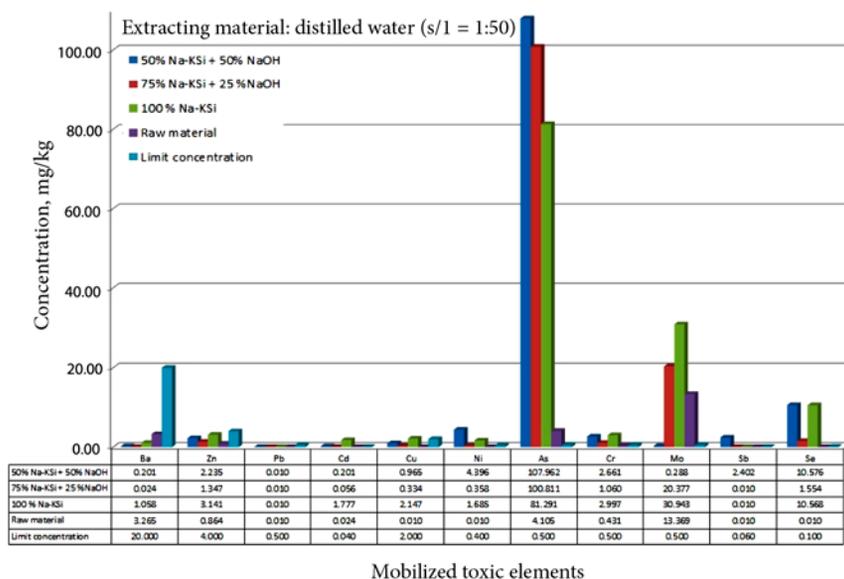


Fig. 12. Quantity of mobilized toxic elements from 120 days age geopolymers using distilled water as extracting material (solid/liquid ratio 1:50)

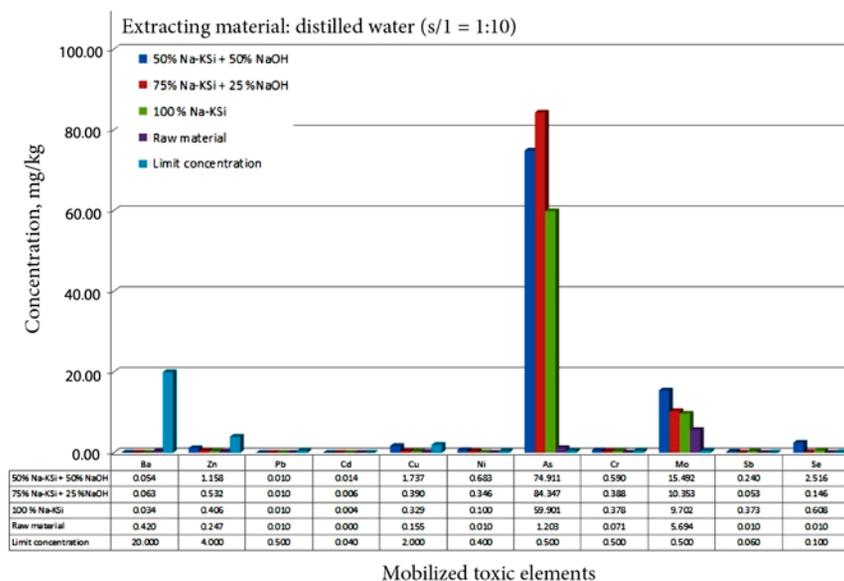


Fig. 13. Quantity of mobilized toxic elements from 120 days age geopolymers using distilled water as extracting material (solid/liquid ratio 1:10)

- The result of the geopolymerization reaction can be indicated by FT-IR, several new peaks appear in FT-IR spectra. It clearly proves the structural rearrangement.
- The leaching using 1 M acetic acid and 1 M hydrochloric acid has revealed that the Si, Al, Fe and Ca are built well in the structure of mechanically activated fly ash based geopolymers.
- The leaching results of toxic elements meet the criteria of the limit concentrations concerning inert landfills except As, Mo, Se.
- After 120 day ageing the quantity of mobile As and Mo increases, the quantity of Se is almost the same as after 10 day ageing. The Cd, Ni and Cr appear also in the aqueous phase, but Pb leaching was not detected.
- The quantity of leachable As significantly exceeds the limit concentration concerning inert landfills. This amount can be moderated by decreasing the residual alkali content.
- The aim of our future research is to decrease the As leachability by optimizing the alkali activator and adding components mobilizing that element in order to moderate the environmental impact.

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