



# High energy density milling as a tool for improving the properties of fly ash based geopolymer

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## ABSTRACT

Generally, fly ash particles are very fine ( $< 100 \mu\text{m}$ ), mainly spherical and glassy materials form an outer shell on it. 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.

The preparation of fly ash using high energy density milling is presented. Systematic experimental series were carried out in order to optimize the preparation process. The particle size distribution (LPSA) and structure of fly ash (FTIR) and the uniaxial compressive strength, the permeability and structure of geopolymer product, furthermore the rheology of geopolymer paste were investigated. The product properties were studied as a function of the fly ash fineness.

As a result of the investigation the relationship between the grinding circumstances, the ground material properties and the geopolymer characteristics was identified. It was found that the above mentioned physical properties of the geopolymer strongly depend on the grinding process.

## INTRODUCTION

Geopolymers are new kind of building materials that can be produced by reaction between alumino silicate oxides and alkali silicates in alkaline medium. Every material are suitable for geopolymer production which contains silica and alumina barrier phases, like natural rocks or secondary raw materials, such as fly ash, slag or even red mud (Davidovits, 1994; Palomo, 1994). The main disadvantage of industrial wastes for geopolymer production is its low reactivity, which can hinder the geopolymerisation reaction and yielding a product with low mechanical strength. The reactivity of fly ash depends on its particle size distribution, specific surface area and mineral phases, including amorphous phases (Kumar & Kumar, 2011, Kumar et al. 2007 a and b).

There are many possibilities to enhance the reactivity of starting material, like mechanical and/or chemical activation. The positive effect of mechanical activation on bulk and surface properties are well known and accepted. Due to the grinding smaller particle size and higher specific surface area was reached, while XRD spectra shows smaller and broader crystal peak intensities and higher glassy phase content. The FT-IR spectra peaks are also changed (Kumar & Kumar, 2011, Kumar et al. 2007 a and b). The mechanical properties (compressive and flexural strength) of ground fly ash based geopolymer are better than that of prepared from raw fly ash. In this paper mechanical activation was used to alter the properties of the geopolymer final product.

## METHODOLOGY, MATERIALS

The lignite-type fresh fly ash collected from Mátra Power Plant, Visonta (Hungary) had been ground and investigated in geopolymer production and FTIR measurements. Raw fly ash - has been characterized using standard techniques and displayed the following physical and chemical properties. The moisture content (4.28 m/m%) was measured by drying fly ash in drying cabinet at 105 °C till reach constant weight. The particle density of the raw fly ash was 1.88 g/cm<sup>3</sup> and bulk density (in dried conditions) was 0.663 g/cm<sup>3</sup>. Particle size distribution and specific surface area was measured by Horiba LA950 V2 type laser particle size analyzer and the value of the specific surface area was 1529.2 cm<sup>2</sup>/g and the characteristic particle diameters were  $x_{50}=31.84 \mu\text{m}$ ,  $x_{80}=90.11 \mu\text{m}$ .

The chemical composition of the fly ash was measured by Rigaku Supermini 200 type X-ray fluorescence spectrometry (XRF). From the analysis the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio was found to be 2.73. The combined SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> content of the fly ash was 74.72 wt%. The main mineral phases (quartz, mullite, cristoballite) were determined by a Bruker D8 Advance XRD apparatus.

Mechanical activation experiments carried out by a custom designed disc stirred media mill with ceramic lining, using the following grinding parameters; rotor circumferential speed (v) 5 m/s, grinding media filling ratio 60 V/V%, material filling ratio 70 V/V%. Durations of the grinding experiments were 1, 3, 5, 7, and 10 minutes respectively. In the case of every grinding experiment energy consumption of the mills' engine was measured by a Carlo Gavazzi 70 type energy-meter.

Geopolymer specimens made by mixing raw- and ground fly ash and caustic soda using 40 m/m % activator solution (in fly ash activator solution mixture). Mixtures were placed into 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 the specimens were cooled down to ambient temperature. The mechanical test was carried out by Compression Testing Machine in 7 days age.

Two parameters had been changed to optimize the geopolymer paste mixture. In each series the chosen optimum value remained and carried on the followings. Varying parameters during systematic geopolymer investigation were grinding time of fly ash (0, 1, 3, 5, 7, 10) and molar concentration of NaOH activator solution (6, 8, 10, 12 mol/l).

Fourier Transformed Infrared Spectroscopic measurements of fly ash and geopolymer specimens carried out by JASCO FT-IR 4200 type Fourier Transformed Infrared Spectrometer in reflection mode, diamond ATR was used. 3 spectras made from each samples.

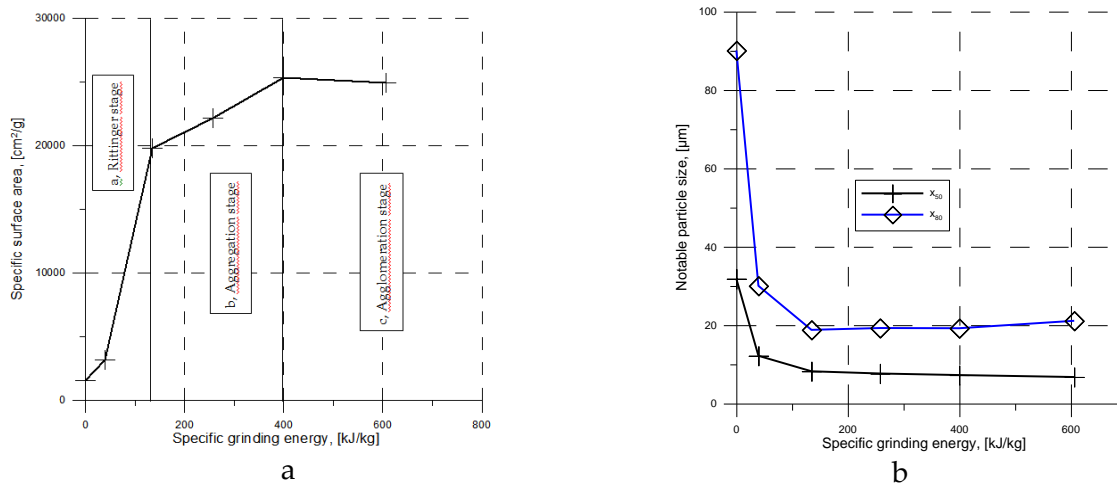
Rheology of geopolymer paste was measured by Anton-Paar Physica MCR51 type rotational viscometer.

A water permeability test was carried out in a permeabimeter with flexible wall. A pressure of 30 kPa was applied to the samples. The permeability was calculated by applying Darcy's Law. The geopolymer specimens for water permeability measurement were made from fly ash ground for various times using 6 M NaOH. The specimens were treated at 60 °C for 6 hours.

## RESULTS AND DISCUSSION

### Mechanical activation of fly ash

The changes of fly ash specific surface area (SSA) as function of specific grinding energy are shown in Figure 1.(a).



**Figure 1.** Changes of SSA (a) and 50 %; 80 % particle size (b) as function of specific grinding energy

The increase of specific surface area is high in the starting (a, Rittinger) stage of grinding process (from initial SSA=1529.2 cm<sup>2</sup>/g by 134.64 kJ/kg specific grinding energy input increased to 19797.87 cm<sup>2</sup>/g). The relationship between specific surface area and specific grinding energy was linear. Increasing of the specific surface area became slower in aggregation stage, b, while the agglomeration stage had been reached, c, after it further increasing was not observed, but minimal decreasing (10 minutes ground sample). 25332.44 cm<sup>2</sup>/g maximum specific surface area was achieved by 400 kJ/kg specific grinding energy, (after 7 minutes grinding).

The changes of 50 % and 80 % passing particle size as function of specific grinding energy can be seen in Figure 1.(b). The Figure shows high decreasing of the particle size values at the beginning part of grinding process till 134.64 kJ/kg energy input, at this point the median was 8.25  $\mu\text{m}$ ,  $x_{80}$  was 18.82  $\mu\text{m}$ . As a result of further energy input the median and  $x_{80}$  particle size values remain nearly constant.

### FTIR results of activated fly ash

It can be seen from raw fly ash spectra (Figure 2), that significant absorption observed at wavenumber 1100, 1020, 797, 675, 610  $\text{cm}^{-1}$  and 594  $\text{cm}^{-1}$  corresponds to T-O-Si (T=Si, or Al) assymetric and symmetric stretching vibrations. Peak at 1414  $\text{cm}^{-1}$  belongs to O-C-O bonds stretching vibration refers to the presence of carbonate in fly ash.

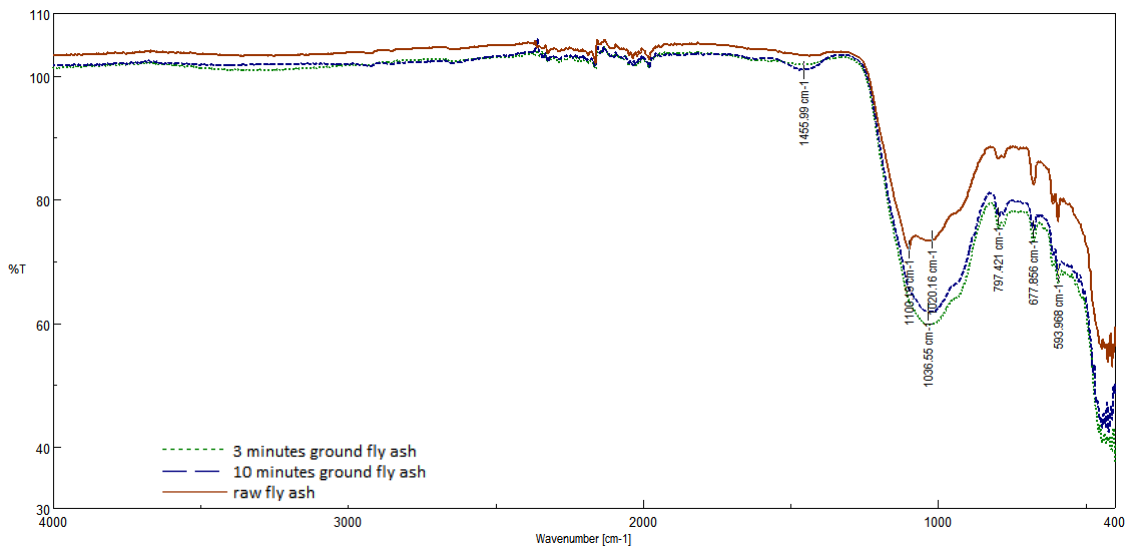


Figure 2. FTIR spectras of raw and ground fly ash

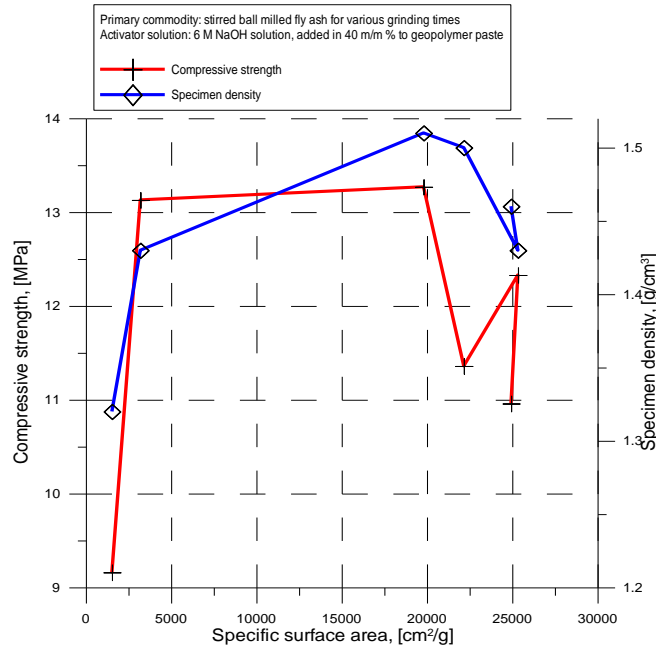
The peaks occurred at 1100  $\text{cm}^{-1}$  and 1020  $\text{cm}^{-1}$  in case of raw fly ash was changed in ground fly ash samples. First was disappeared second shifted to 1036  $\text{cm}^{-1}$  (T-O-Si T=Si/Al assymetric stretching vibration). Peak at 610  $\text{cm}^{-1}$  also disappeared. Disappearance of peaks at 1100 and 610  $\text{cm}^{-1}$  might have resulted due to **structural changes** in fly ash due to grinding. Increase in the residence time (grinding time) has no effect on structure.

### Mechanical properties of geopolymers

The main mechanical properties which indicates the result of geopolymerisation is its compressive strength and context with its specimen density.

### Effect of fly ash fineness

Particle size distribution measured by Horiba LA 95 V2 type laser particle size analyser (LPSA), specific surface area calculated of particle size distribution datas using shape factor 1.

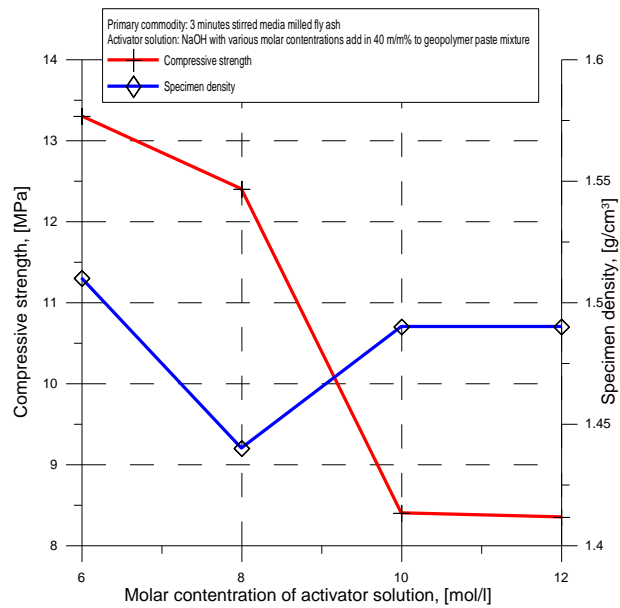


**Figure 3.** Changes of compressive strength and specimen density as function of fly ash specific surface area

It can be stated that geopolymer specimen made using raw fly ash with 1529 cm<sup>2</sup>/g specific surface area resulted only 9.16 MPa compressive strength, while 3 minutes ground fly ash (19798 cm<sup>2</sup>/g) based geopolymer reached 45 % higher compressive strength (13.3 MPa). Similar to compressive strength the specimen density has also increased by increasing the fly ash fineness.

### Molar concentration of NaOH solution

The activator solution with higher molar concentration resulted lower compressive strength (Figure 4.). This is in contrast with literature and need further investigation to explain the main cause.



**Figure 4.** Changes of compressive strength and specimen density values as function of activator NaOH molar concentration

Since the main reactive component of fly ash (glassy phase) was low, the requirement of alkali quantity for geopolymerisation was small. Thus higher concentration solution resulted into excess alkali, which continued the dissolution precipitation reaction of some fraction and thus polycondensation process was not complete. In the case of various concentrated NaOH solutions experimental series, compressive strength decreased by higher NaOH concentration unlike experimental data found in literature. It needs further structural investigations to detect the cause of this anomaly.

#### *FTIR results of fly ash based geopolymers*

Due to geopolymerisation new peaks were observed and shifted to lower wavenumber, some remained the same. Peaks at 3356 cm<sup>-1</sup> related to -OH, HOH bonds stretching vibration, at 1638 cm<sup>-1</sup> corresponds to HOH bending vibration. Peak at 1398 cm<sup>-1</sup> belongs to O-C-O stretching vibration. The peak appear at 1036 cm<sup>-1</sup> in case of raw fly ash shifted to lower wavenumber (950 cm<sup>-1</sup>), its intensity is also increased and supplemented by a peak at 1091 cm<sup>-1</sup>. This peak can hardly observed in case of activated system by 6 molar NaOH solution, but increasing activator solution NaOH concentration its intensity also increased. This indicates structural reorganisation, and amorphous aluminosilicate gel formation. It is associated with dissolution of the amorphous phase of fly ash due to strong alkali media according to Panyas et al. (2007). It can be stated, that all peak intensities increased by increased NaOH content of activator solution.

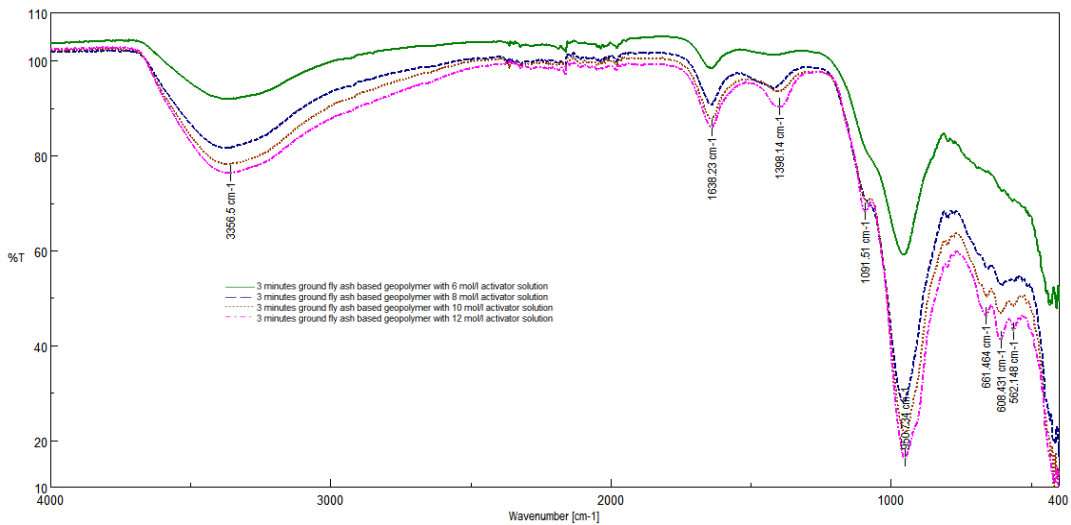


Figure 5. FT-IR spectras of geopolymer specimens made by various concentratrtd NaOH solution

Peaks at 800, 661, 608 and 562  $\text{cm}^{-1}$  related to Si-O-Si and Al-O-Si symmetric stretching vibration. These peaks can hardly observed in case of fly ash which activated by 6 mol/l NaOH activator solution, while peak intensities increased, by molar concentration of NaOH solution.

### Unpermeable properties of geopolymer

The permeability coefficient as a function of the specific surface area of the raw material fly ash can be seen in Figure 6.

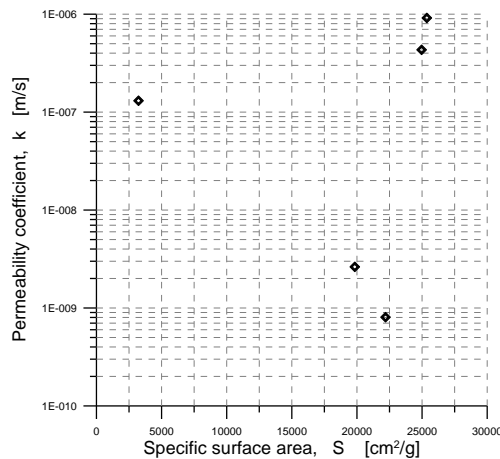


Figure 6. Permeability coefficient of the geopolymer as a function of specific surface area of the raw material fly ash

Higher specific surface area resulted in lower permeability. The lowest coefficient was reached around 22500 cm<sup>2</sup>/g fly ash specific surface area with a value of 8.14E-10. At higher specific surface area the permeability coefficient of the geopolymer specimen became significantly worse.

### Viscosity of geopolymer paste

It can be stated, that in the case of raw fly ash and water mixture (when solid/mixture mass ratio was 0.45, while solid/mixture volume ratio was 0.39) has bingham plastic rheology. Coefficient of rigidity was 0.0926 Pa·s and yield stress was 7.42 Pa.

In all other cases of NaOH solution fly ash mixtures (when solid/mixture mass ratio was 0.45, while solid/mixture volume ratio was 0.44), the rheology were also bingham plastic (Figure 7, a). The yield stress of fly ash, NaOH activator solution mixtures decreased by increasing of specific surface area (grinding time) (Figure 7, b). The decrease was significant after 1 minute grinding time compared to raw fly ash.

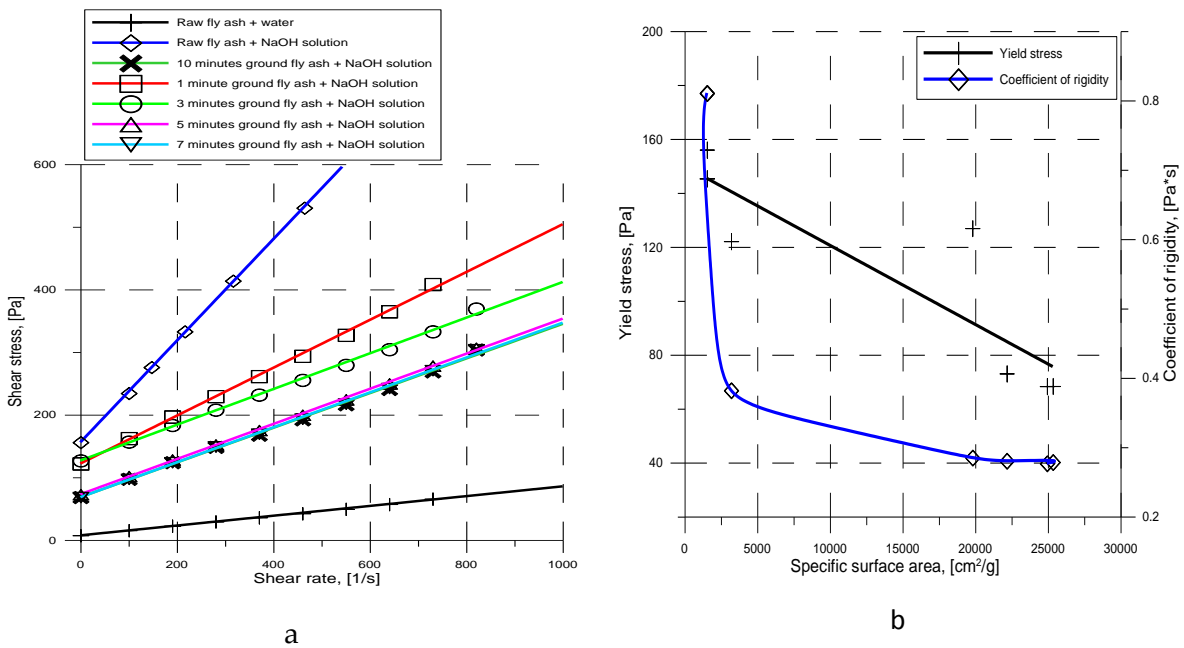


Figure 7. Rheology of geopolymer paste

In 1 and 3 minutes ground fly ash, activator solution mixtures shows similar Yield stress. Significant decrease in Yield stress was observed after 5 minutes grinding time, after that the decrease was minor. With increase in grinding time the coefficient of rigidity of NaOH solution decreased. The rate of decrease was very high when grinding time was low and reached to steady state after 3 minutes grinding. Further decrease was hardly observed.



## CONCLUSIONS

Maximum specific surface area of 25332.44 cm<sup>2</sup>/g was achieved by 400 kJ/kg specific grinding energy (after 7 minutes grinding). However, optimum compressive strength value belongs to 3 minutes ground fly ash (SSA= 19797.87 cm<sup>2</sup>/g) based geopolymer.

Higher NaOH concentration of activator solution resulted in lower compressive strength, which is in contrast with the literature. The optimum value was reached by 6 mol/l concentrated NaOH solution.

Investigations of geopolymer paste viscosity shows bingham plastic rheology, when activator solution was 6 mol/l NaOH solution. Increasing the fineness of the fly ash the yield stress and plastic viscosity also decreased.

The water permeability of the fly ash based geopolymer can be controlled by grinding in the range of 10<sup>-6</sup> down to 10<sup>-10</sup> m/s permeability coefficient (k).

## ACKNOWLEDGEMENTS

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