

# **Geopolymers – in environmentally friendly aspects**

Thesis for the master degree  
Material Science MSc

**KÓTH JÁNOS**

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## The goal of the study

Geopolymers belong to the family of inorganic polymers, which are macromolecules linked by covalent bonds and having -Si-O-Metal-O- backbone. According to the definition of Davidovits, the geopolymers consist of a polymeric silicon-oxygen-aluminium framework with alternating silicon and aluminium tetrahedra joined together in three directions by sharing all the oxygen atoms. The tetrahedron aluminium possesses a negative charge and therefore the presence of cations such as  $K^+$  and  $Na^+$  is essential to maintain electric neutrality in the matrix. By new terminology the geopolimeric structures are described as: (1) poly(sialate) with [-Si-O-Al-O-] as repeating unit, (2) poly(sialate-siloxo) with [-Si-O-Al-O-Si-O-] as repeating unit, and (3) poly(sialatedisiloxo) with [-Si-O-Al-O-Si-O-Si-O-] as repeating unit. The geopolymers are commonly used as coatings, adhesives, structural, and constructive materials. To enhance this attractive quality of the geopolymers, a number of studies were conducted to use industrial waste products as precursor materials [1,2].

One of the goals of the present research was to create geopolymers with good mechanical properties. The other one was the recycling of the industrial waste materials with respect of the environmentally friendly purpose. The very dangerous, toxic red mud as mine waste was selected for recuperation. Regarding the requirement of low energy consumption, the sol-gel method was applied to produce the geopolymers.

During previous researches in the Sol-gel Laboratory of ELTE, aluminium-silicate systems were synthesized starting from Alnitrate, isopropoxide or acetate as Al-precursor, and tetraethoxysilane or sodium-silicate as Si-precursor [3]. The newly developed sol-gel method, proved to be an easy, reliable and low cost, low energy consumption procedure. This sol-gel preparation is based on the basic dissolution of aluminium-acetate and sodium-silicate. By using organic aluminium source, the environmental damages *e.g.* the escape nitrates as nitrous gases can be avoided. Thus, the organic anions, *i.e.* acetate ions can be decomposed into water and carbon-dioxide during the reaction and the heat treatment. The sodium-silicate (water glass) was chosen due to its relatively low cost and its sodium ion content. Above all,  $Na^+$  ions have a role in the structure of geopolymers in the help of aluminium ions to build into the silicate structure, as tetrahedron  $AlO_4^-$  ions. In this research the recreation of the samples was aimed by means of the previous experiments, and modification of the original recipe to use red mud in the geopolimeric materials. My tasks were to optimize the preparation conditions, such as the amount of base materials, solvents, the red mud, and the specifications of the heat treatment.

The tasks also involved the characterization of the resulted geopolymeric samples, through NMR-MAS spectroscopy, X-ray powder diffraction, thermoanalytical investigation techniques, the mechanical strength and solubility measurements, complemented with ICP-MS method.


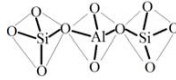
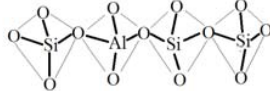
# I. Introduction

## I.1. Geopolymers

The first geopolymers were developed in the 1950-ies under the name “soilcement” in the Soviet Union, by Viktor Glukovsky. Two decades after, in 1972 Joseph Davidovits coined the term “geopolymer” for three dimensional aluminium-silicates, which are produced from natural alumina-silicates on low temperature and ambient pressure. [4] In modern construction industry they were recognized as a potential new environmental friendly alternative to traditional structural materials. The cheap raw materials, the low energy consumption of the preparation methods and the potential recycling of industrial waste make geopolymers an attractive, environmentally friendly solution for many problems of the industry.

Today geopolymers are used as an overall term for aluminium-silicate polymer systems, which also includes systems with other metal ions, such as alkaline, or alkaline earth metal ions. The geopolymers can be divided into natural and synthetic products. The most natural geopolymers are clay minerals, such as kaolinite or illite. The structure of geopolymers are generally amorphous or semi-amorphous. The silicate network consists of interlinking  $\text{SiO}_4^-$  and  $\text{AlO}_4^-$  tetrahedrons, by sharing every oxygen atom. The structural holes are filled by cations, such as  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Ca}^{2+}$ , which stabilize the structure, by balancing the negative charge  $\text{AlO}_4^-$  ion. [5,6] The chemical composition can be characterized by the following simple empiric formula:  $\text{M}_n(-(\text{SiO}_2)_z-\text{AlO}_2)_n \cdot w\text{H}_2\text{O}$ , where  $M$  is a cation with one positive charge,  $n$  is the degree of polycondensation and  $z$  is an integer, with a value of 1.2 or 3.0.

Table 1. The structure of geopolymers

Si/Al molar ratio	Polysialate type	Schematic structure	Spatial structure
1	Polysialate	$(-\text{Si}-\text{O}-\text{Al}-\text{O}-)$	
2	Polysialate-siloxo	$(-\text{Si}-\text{O}-\text{Al}-\text{O}-\text{Si}-\text{O}-)$	
3	Polysialate-siloxo	$(-\text{Si}-\text{O}-\text{Al}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-)$	

We can also use the  $\text{Q}_n(\text{mAl})$  formula, where  $Q$  is the central atom,  $n$  is the coordinational number of the centre and  $m$  is the number of neighbouring aluminium atoms, that connect

through the oxygen to the central atom. The value of n and m are between 0 and 4. In Figure 1. the different structural variations of the silicon tetrahedrons can be seen, while the 3D structure is represented in Figure 2.

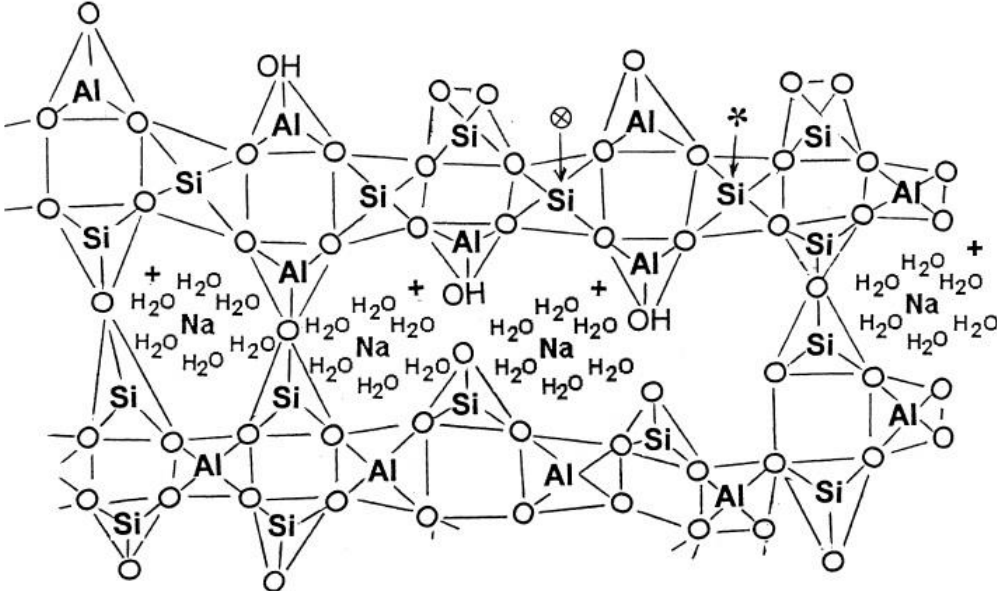


Figure 1. The schematic structure of Na-polysialate [7]

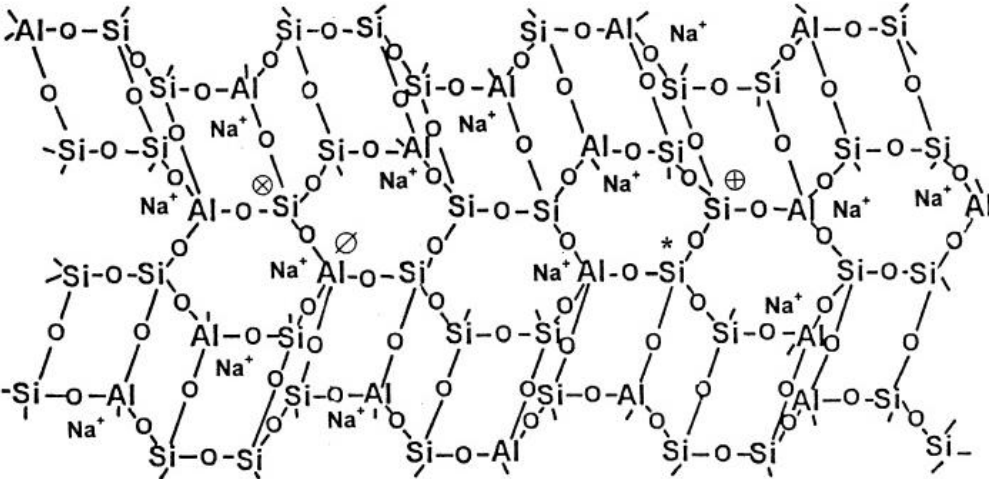
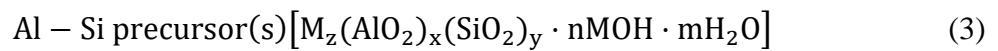
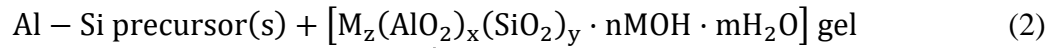
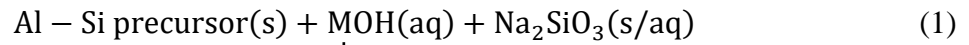


Figure 2. The 3D structure of geopolymers [7]

**I.2. Preparation of geopolymers**

The versatility of the synthesis methods is another point of interest for the geopolymers. The precursors may be synthetic molecules, salts; aggregates of natural clay minerals, perlite, feldspar; furthermore, fly ash, slag or red mud as industrial wastes. Although there are both acidic and basic routes to synthesize geopolymers, when recycling the mentioned wastes,

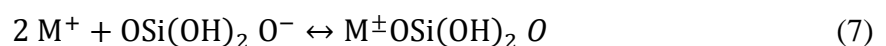
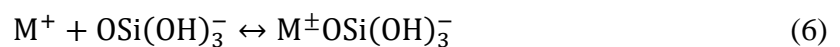
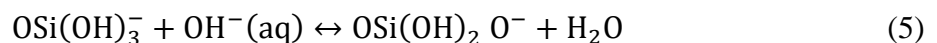
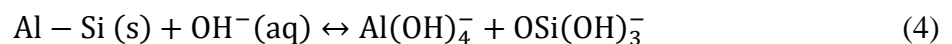
generally the basic route is preferred using sodium- or potassium-hydroxide solution. The following chemical equations were proposed for the polycondensation during the geopolymerisation in such medium [8]:

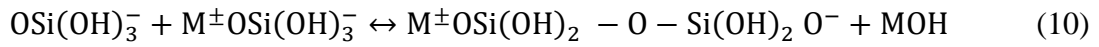
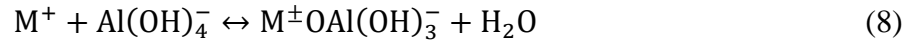


The dissolution of the precursors is the determining step regarding the structure, with dual roles in the reaction. The polysialate compounds are released from the precursors and the dissolution activates the surface, which starts the reaction leading to the formation of bonds. The amount of natural aluminium-silicate incorporated depends on the solubility of the aluminium silicate, its grain size and the concentration of the basic solution.

Xu and coworkers investigated 16 natural aluminium silicate minerals, such as sodalite and illite, regarding their geopolymerization processes [8]. The materials were milled and dissolved in a sodium or potassium hydroxide medium. The chain-structured materials, such as augit can be dissolved better in the basic solutions, than the ones with 3-D network structure, such as sodalit. This shows, that natural aluminium-silicate minerals are suitable precursors for geopolymers, but doesn't prove, that all clay minerals are possible to use. The investigation of compressive strength shows that using minerals with higher degree of solubility leads to harder samples. Furthermore, the materials prepared using KOH possess higher compressive strength, than the ones dissolved in NaOH.

Dissolution of aluminium-silicate minerals in strong basic medium [9-11]:





Thus the geopolymerization can be divided into 4 steps [12-16]:

First the metal ions on the surface are coordinated by water molecules, creating silanol and aluminium-hydroxide groups. In the solution, aluminium and silicon ions are released, creating tetrahedral hydroxide complexes.

As a second step, oligomers are formed in the aqueous phase, and the concentration of tetrahedron Si and Al ions increases. The oligomers are built up from Si-O-Al and Si-O-Si bonds.

In the third step, a three dimensional structure is formed. The 3D network grows from SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedrons attached by oxygen atoms.

The structure is completed, as the oligomers can react with all OH-containing units, creating chains, rings or 3D structure. In this step, the oligomers can form bonds with eachothers, hardening the geopolymeric systems by crosslinking connections.

One of the new synthesis routes for geopolymers today is the sol-gel technique. The sol-gel technique was created to replace classic, high temperature melt technologies. It has low energy and temperature requirements, which can be used to produce new materials with tailored structures. The process can be regulated through multiple experimental factors, such as pH, catalisators, temperature, and other additional materials. The principle of the technique is to create metal-hydroxide and after that metal-oxygen-metal bonds in the solution and gel phases. The silicon and aluminium alkoxides are usually used as precursors in a alcohol-water mixture. The first step is the basic or acidic hydrolysis of the alkoxide groups, creating hydroxile groups. Next step is the condensation reaction, which leads to the production of oligomers and polymeric 3D network in the whole volume of the solution. Basic or acidic medium is used to fasten the reaction speed. In an acidic solution, the hydrolysis is dominant, resulting a looser structure, while in a basic system the condensation is dominant, producing a more compact structure.



The additional aim of the aluminosilicate sol-gel experiments were to develop a technique, which could produce a higher aluminium content in the silicate network, than materials produced with classical melting technology. [17-19]

The next phase after the gel formation is the aging. This process is suitable for the modification of the gel structure and thus the characteristics of the material. The final step of the sol-gel technique is the drying and the heat treatment. [20]

The biggest problem of producing aluminosilicate monoliths, is the drying step. During the drying the escape of solvent, causes shrinkages, which can lead to crack the monolith structure. [21,22] To prevent this, the gel is dried slowly at atmospheric pressure or use other techniques, such as supercritical drying. The wet gels' strength can increase significantly during the ageing.

In Figure 3. a general sol-gel production method can be seen. The precursors are mixed with an activator solution, thus forming an alkaline-aluminium-silicate gel. The activator contains both alkaline and hydroxide ions [23]. The additional aim of the aluminosilicate sol-gel experiments were to develop a technique, which could produce a higher aluminium content in the silicate network, than materials produced with classical melting technology.

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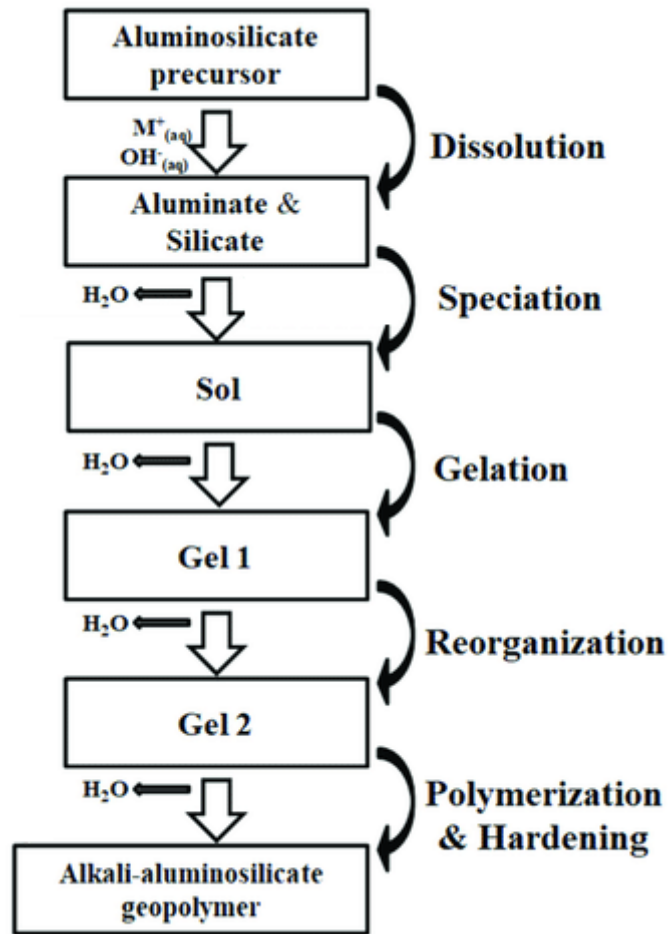


Figure 3. The formation of geopolymers from precursors [24]

### I. 3. Recycling of red mud

One of the most problematic industrial waste materials is the red mud. It is dangerous to the environment, due to its highly basic nature. The generally the containment is more cost effective than the neutralization process. On average 120 million tonnes of red mud produced every year, thus the storage means an ever increasing challenge. At this moment, the majority of researches concentrates on metallurgical procedures and the production of building materials. [25]

The metallurgical procedures aim is to recover raw materials from the red mud. Due to the iron oxide presented in a substantial amount together with TiO<sub>2</sub>, the red mud is suitable for these materials' recovery. However, a sintering process is required to neutralise the effect of high Na<sub>2</sub>O and aluminium content. Secondary constituents, such as rare earth elements have also been recovered, for example, Sc or Y. [26]

Red mud has been used in building materials such as glass-ceramic, ceramic pigments, ceramic foam [27, 28, 29, 30, 31], fire resistant building materials [32], cement and block production [33, 34, 35]. Their use in geopolymer production has also been investigated, as precursors, due to its aluminium and silicon content.

In some literature the effect of the red mud's amount on geopolymer is not advantageous, as the mechanical properties of the binder deteriorated when the ratio between red mud and other materials increased [36]. The lower red mud content generated a positive effect on mechanical properties (ductility, stiffness and strength) of geopolymer, [37, 38]. That poses a challenge to the research of their application in geopolymer production.

#### I. 4. Characteristics and applications of geopolymers

Geopolymers are excellent protective coating materials, due to their fire and heat resistance [39]. Furthermore, they have low water permeability and low deformation. Table 2. represents their various application, based on the structure and the precursor ratio.

Table 2. The application of geopolymers with different precursor ratios [40]

Si/Al ratio	Polymeric character	Applications	
		Low technology	High technology
Si:Al=1:1	3D Network	- Tiles - Ceramics - Fire protection	
Si:Al=2:1		- Cements - Concretes - Radioactive and toxic wastes management	
Si:Al=3:1	2D Cross-link	- Foundry equipment - Fire resistant fiber glass composites	- Tooling for aeronautics - Heat resistant composites
Si:Al>3:1		- Sealants for industry	- Tooling for aeronautics
20:1<Si:Al and Si:Al>35:1			- Fire and heat resistant fiber composites

Their primary field of the application is in the construction industry. They are applied as fire resistant coating for wallboards or replacement of cement [41]. They were also tested as adhesive materials due to their applicability on higher temperatures and low preparation costs [41]. Geopolymer composites are produced to replace plastic components. In airplanes, carbon-nanotube strengthened geopolymers are applied to avoid the flammable and poisonous gases released from burning plastics in a case of fire or accidents [41]. Due to their long-term chemical resistance, they can be used to store radioactive or toxic materials, which can not be escaped from the geopolymeric matrix [42]. This is one of the most promising fields of research.

The geopolymers can also be used in therapeutic fields, one such example is the synthetic kaoline [43]. Geopolymeric composites based on kaoline and calcium-phosphate are biocompatible and can be used as base material for synthetic bones. These application have strict medical requisites; thus traditional production methods are not suitable for these challenges.

## **II. Investigation methods**

During my research I prepared aluminosilicate systems with sol-gel method and investigated in the relation to composition, precursor ratios and heat treatment. The samples were investigated using  $^{27}\text{Al}$  MAS NMR spectroscopy, X-ray diffraction, ICP-MS analysis, thermoanalytics, and the solubility and the hardness measurements.

### **II. 1. Preparation of the samples**

I used basic aluminium acetate (Alfa Aesar and Acros Organics) and sodium silicate (Sigma Aldrich) as synthetic precursors. The red mud and the red mud with reduced iron oxide content (RMR) was provided by Bay Zoltán Nonprofit Ltd. for Applied Research. The composition of the red mud and the RMR can be seen in Table 2.1 and 2.2. The synthetic geopolymeric samples were produced by dissolving the aluminium acetate and the sodiumsilicate with a 3:1 ratio in aqueous NaOH solution with an approximately pH=14 on the solution was stirred at 60 °C. The recipe using red mud, differs only so that the aluminium and the silicon content of the red mud is also calculated in the 3:1 ratio, and the red mud is added after the mixture of two synthetic precursors. Red mud can partly be dissolved in the NaOH solution.

The maximum weight of the red mud, that can be incorporated in the aluminosilicate is approximately 33% of the sample's total mass, while the maximum amount is 14% for the red mud with reduced iron oxide content with the respect of the required 3:1 Al/Si molar ratio. The solution was further stirred, for an hour at room temperature, then the main part of solvent was removed. The samples were heat treated at 100 °C for 24 hours in an open cast.

According to the literature examples, the 3 dimensional geopolymeric structure reaches the completion at higher temperatures, around 600 °C. Based on this, I used a final, 4-hours heat treatment for various samples at different temperatures.

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Table 2.1: Composition of red mud, provided by Bay Zoltán Nonprofit Ltd. for Applied Research

Components	Content ( $\frac{m}{m}\%$ )
Fe <sub>2</sub> O <sub>3</sub>	24-45%
Al <sub>2</sub> O <sub>3</sub>	15-28%
TiO <sub>2</sub>	3-11%
SiO <sub>2</sub>	5-20%
Na <sub>2</sub> O	5-12%
CaO	1-3%

Table 2.2: Composition of red mud with reduced iron-oxide content (RMR) provided by Bay Zoltán Nonprofit Ltd. for Applied Research

Al-oxid	10,39%
Ca-oxid	4,11%
Ce-oxid	0,07%
Cr-oxid	0,05%
Fe-oxid	11,52%
K-oxid	0,19%
La--oxid	0,03%
Mg-oxid	0,24%
Mn-oxid	0,10%
Na-oxid	0,89%
P-oxid	0,53%
Sr-oxid	0,04%
Ti-oxid	5,83%
V-oxid	0,04%
Zr-oxid	0,24%
SiO <sub>2</sub> v szilikát	65 % körüli

The maximum weight of the red mud, that we could dissolve in the solution is approximately 33% of the sample's total mass, while it for the red mud with reduced iron oxide content 14% was the maximum with the respect of the required 3:1 Al/Si molar ratio. The solution was

further stirred, for an hour at room temperature, then the main part of solvent was removed. The samples were heat treated at 100 °C for 24 hours in an open cast.

According to the literature examples, the 3 dimensional geopolymeric structure reaches the completion at higher temperatures, around 600 °C. Based on this, I used a final, 4-hours heat treatment for various samples at different temperatures.

## **II. 2. Magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR)**

NMR is a non-destructive structural investigation technique. Its spectrum can be used to analyze the atomic bond within the sample. A liquid helium cooled, superconductive electromagnet is used, create a magnetic field, in which the appropriate elements can be investigated. The samples'  $^{27}\text{Al}$  MAS NMR spectras were recorded in the ELTE's NMR laboratory, using a BRUKER DRX-500 NMR SPECTROMETER (magnetic field 11,744 T), at room temperature, in 4 mm rotor, using 99,36 MHz Larmor frequency. In solid phase NMR, with MAS technique, the sample is rotated with high speed at an  $54,74^\circ$  angle to the magnetic field. This is advantageous anisothrope interactions are significantly averaged. Thus the signals would be sharper and thinner, than in a statical spectra. This also enables the structure of amorphous systems, such as ceramics or glasses, not just crystalline samples.

The samples measured are part of the optimazition process. They were synthetic samples, with samples containing different amount of red mud with reduced iron. Red mud samples were not measured, due to ferromagnetic phase content. The samples were treated at 600 °C in the final heat treatment step.

## **II. 3. Powder X-ray diffraction**

By analysing the position and relative strength of the intensity maxima of diffracted X-rays, the diffracting material's crystal structure can be determined. In the case of powder diffraction, the radiated volume contains a large number of randomly oriented crystal grains. Here, the measured diffractogram's intensity-distribution, doesn't change significantly when the sample is rotated. The measurements were done in the ELTE Physics Institute using a Philips (PW3710) device. The intensity distribution of the diffracted X-rays was measured, versus the the diffraction angle ( $2\theta$ ). The radiation source was an X-ray tube, and the detector was a proportional counter. The measurement is contolled, and its data collected by computer. The starting and ending angles, the detector's step size, and the detecting time were set using a

control program. The computer measures the number of counts in a given detector position, in function of the local coordinates, and stores it in a data file.

The samples were grinded to powder before measurement. These samples were treated at 100°C, 200°C, 300°C, 400°C, 500°C and 600°C. The angle was changed between 5° and 100° with a 0,020° step size. The results were analyzed using databases, such as ICDD and other data from the literature.

## **II. 4. Inductively coupled plasma mass spectrometry**

To investigate the building of the 3D structure, materials dissolved from 600°C heat treated samples were further analyzed using inductively coupled plasma mass spectrometry (ICP-MS) technique. The prepared geopolymer samples, weighing 2-3 grams, were put in 200 ml of distilled water, and left alone for 2 hours. The resulted samples were then filtered, and the filtrate was prepared for ICP measurements, by adding high purity, concentrated nitric acid, to prevent the precipitation of aluminium-hydroxide. The measurement was done at the Analytical Department of the ELTE Chemistry Institute, with a iCAP Q ICP-MS (Thermo Fisher Scientific) device, using quartz sample holders. The concentration values were calculated with 1000 times dilution and measured with *He* collision mode. The set dwell time was 0,05 seconds, with 10 runs and 3 passes.

## **II. 5. Solubility measurement**

I have prepared samples with synthetic and red mud containing recipes, with 3/1 aluminium and silicon ratios, applying heat treatment at 100°C, 200°C, 300°C, 400°C, 500°C, and 600°C. The prepared geopolymer, samples, weighing 2-3 grams, were put in 200 ml of distilled water, and left alone for 2 hours. The resulted samples were then filtered, the residue were then dried and weighed.

## **II. 6. Thermoanalitics**

The weight change of the samples was followed with respect to the temperature by thermogravimetry (TG). TG was employed together with differential thermoanalysis (DTA). The thermoanalytical measurements were done using a Derivatograph-C System device, between 25 °C and 1000 °C, under static air atmosphere, with 10 °C/minute heating rate. The sample holder's material and the reference material was aluminium-oxide. The measurement



was controlled by a computer, connected to the device. The samples of synthetic and red mud containing samples heat treated at 100 and 600 °C. 10 mg was measured from these samples into the sample holder, with one decimal accuracy.

## **II 7. Compressive strength measurements**

The compressive strength of the samples was tested using a Material Testing System 810 device, in low pressure mode. I prepared synthetic and red mud containing samples with final heat treatments at 100-600 °C, and measured the force necessary to compress the samples with a constant rate of 0,01 mm/s. The samples were cylindrical shaped, with 20 mm diameter top and bottom sides, and with heights varying 13-16 mm.

### III. Results and discussion

The slow addition of the waterglass into the concentrated, basic solution of aluminium acetate produces small amount of white precipitate in the solution. In the case of red mud containing samples, some red colored precipitation is also observable. By removing the water content, the precipitate becomes a slurry. After the heat treating the samples at 100 °C and atmospheric pressure, a gel-like aluminosilicate structures can be obtained. These porous, cylindrically shaped samples are formed by a heat treated in the final step, at different temperatures. The final products are samples with different compressive strength and phase composition. The method reliably provides intact monolith structures, without cracking through fast, atmospheric heat treatment. This possibility, *i.e.* a fast, atmospheric drying, which does not result in any cracking, is a unique process in sol-gel technique. This drying process, the low energy consumption, and the special nanocomposite product provide the important novelty for the developed sol-gel procedure. The special nanocomposite structure is provided by a special molar ratio of Al/Si. The published Si/Al molar ratios are between 1 and 5. (See Table 2.) Our applied molar ratio: 1:3 Si/Al. This molar ratio has a very important role according to the previous experiments in the Sol-gel Laboratory.

#### III. 1. Structure of geopolymers

##### III. 1.1. Magic angle spinning nuclear magnetic resonance spectroscopy

Fig. 1 represents NMR spectra of samples with different - reduced iron oxide containing - red mud content. There is one main peak at 78.7 ppm and multiple wider peaks at the range of 60-75 ppm. The sharp peak shows the presence of a crystalline phase containing aluminium in tetrahedral co-ordination [45]. The wide peak at 63.8 ppm indicates an amorphous aluminium-silicate 3D network [46]. The NMR spectra confirm composite structures, where the crystalline phase is embedded in the amorphous network. The peak at 68.7 ppm, as the sum of two peaks, show the presence of a zeolite phase, also with tetrahedral aluminium content [47]. Zeolites possess polymeric Si–O–Al framework, similar to geopolymers, but predominantly with crystalline structure. The peak at 86.4 ppm belongs to a calcium-aluminium-silicate phase [48]. These samples have poor structural stability and hardness. In addition, the <sup>27</sup>Al MAS NMR is also different from the previous NMR spectra (Fig. 2). The reason of the difference was found to be the incorrect crystalline water content of Al acetate precursors. Thus, that resulted in less

Al/Si molar ratio than the required value. The recipes had to be revised to achieve the 3:1 Al:Si ratio. The new samples haven't been tested due to failure of NMR instrument.

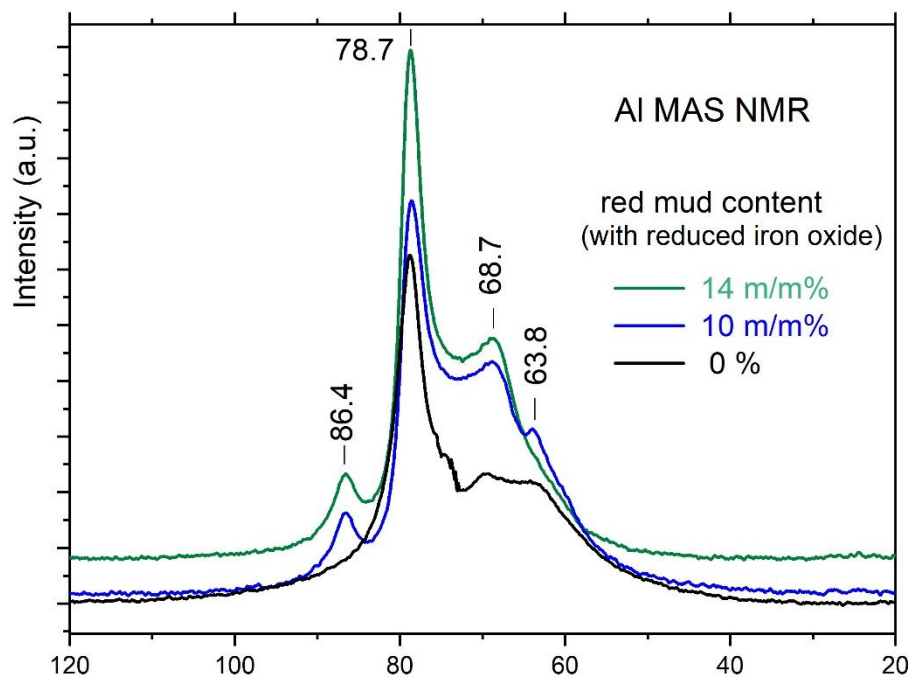


Figure 1. The  $^{27}\text{Al}$  NMR spectra of samples heat treated at 600 °C, in the function of reduced iron oxide containing red mud content

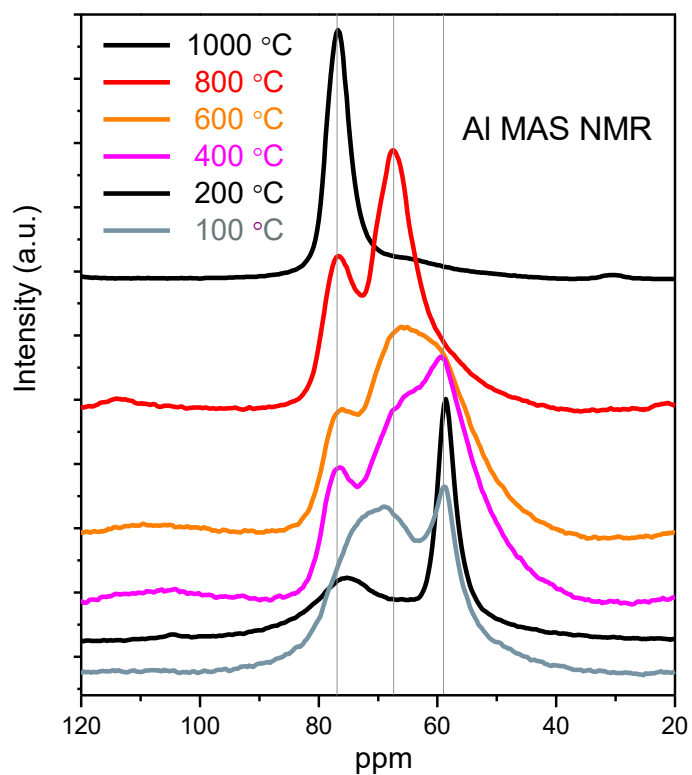


Figure 2. Previous  $^{27}\text{Al}$  NMR spectra of samples prepared from synthetic precursors.

### III. 1.2. Powder X-ray Diffraction

The aim of the X-ray powder diffraction measurements was to better understand the structural changes in the samples during the heat treatment. In Figure 3 and 4 the X-ray spectra of the synthetic samples can be seen in the function of heat treatment' temperature. Between 300 °C and 400 °C there are important phase changes, which result in very different spectra for samples treated above and below 300 °C (Fig. 3 and 4). The identification of the crystalline phase was difficult, as the geopolymer samples can be characterized by new composition and the newly developed phases are not highly ordered.

According to PXRD data, the sodium-aluminium-silicate phase is an amorphous, geopolymeric phase, the other dominant phase is the P-type zeolite phase 1., which has very high intensity peaks. We can also see the presence second zeolithic phase, and a gamma aluminium-oxide phase. The intensity of the main phases shows no obvious tendency in the function of temperature. On the other hand, comparing Figure 3 and 4 obvious differences can be observed. The peak around 17.75° disappears at the higher heat treatment temperatures. That indicates the first zeolite structure goes through phase transformation. The second zeolithic phase shows no a strong tendency in the function of temperature, some increase of peak intensity is proved by PXRD. Not only the geopolymeric phase but the other crystalline phase, *i.e.*  $\gamma$ -aluminium oxide phase shows increasing intensity as the temperature of the heat treatment grows.

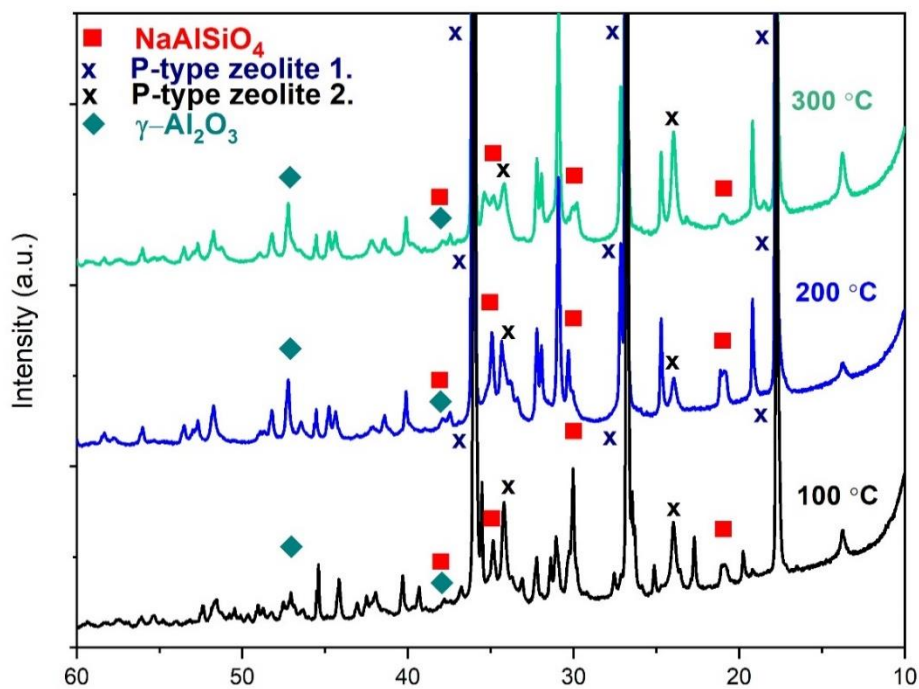


Figure 3: The X-ray powder diffraction spectra of synthetic samples heat treated on 100 °C, 200 °C and 300 °C

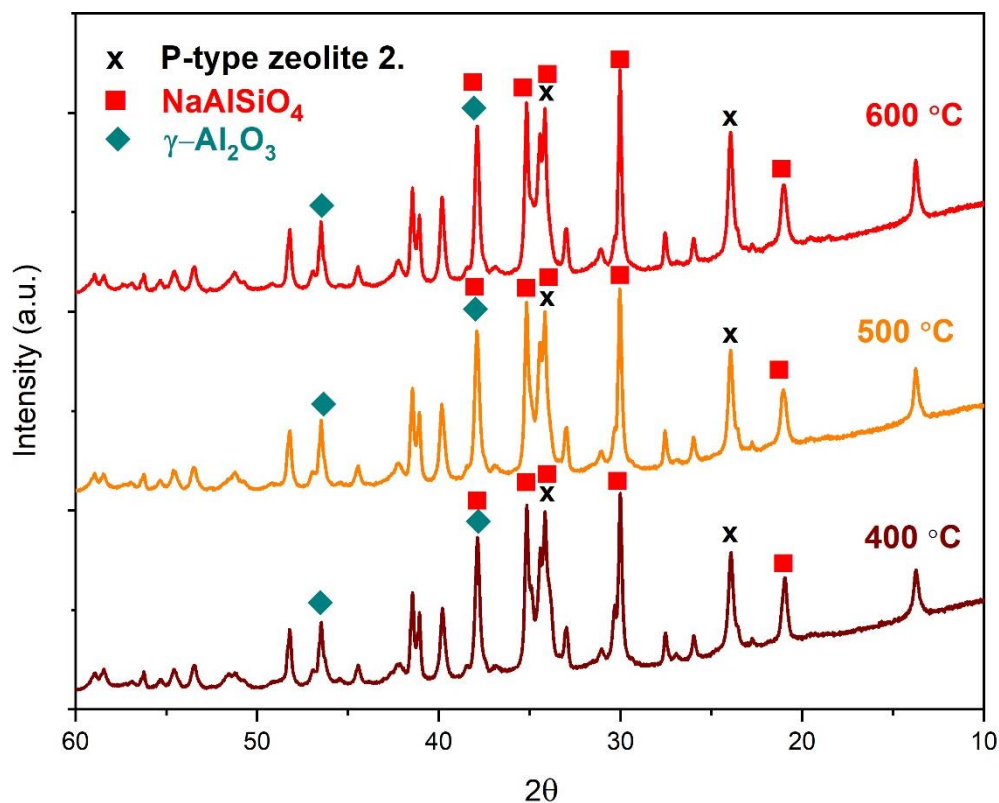


Figure 4: The X-ray powder diffraction spectra of synthetic samples heat treated on 400 °C, 500 °C and 600 °C

The X-ray diffractograms of the red mud containing samples can be seen on Figure 5 and 6. Similar tendencies and changes can be observed on the XRD diffractograms as on the synthetic samples' spectra. The P-type zeolitic phase 1 transforms again above 300 °C. The intensity of the NaAlSiO<sub>4</sub> phase increases in the function of temperature up to 300 °C, above that it retains the intensity. The intensity of the other zeolitic phase (P-type zeolitic 2) doesn't change significantly. The non-zeolite phases show higher peaks on the higher heat treatment (Fig. 5, 6). The calcium-aluminium-silicate phase, indicated by the NMR, was not identified, due to the lack of matching pattern in the database or the literature during the analysis.

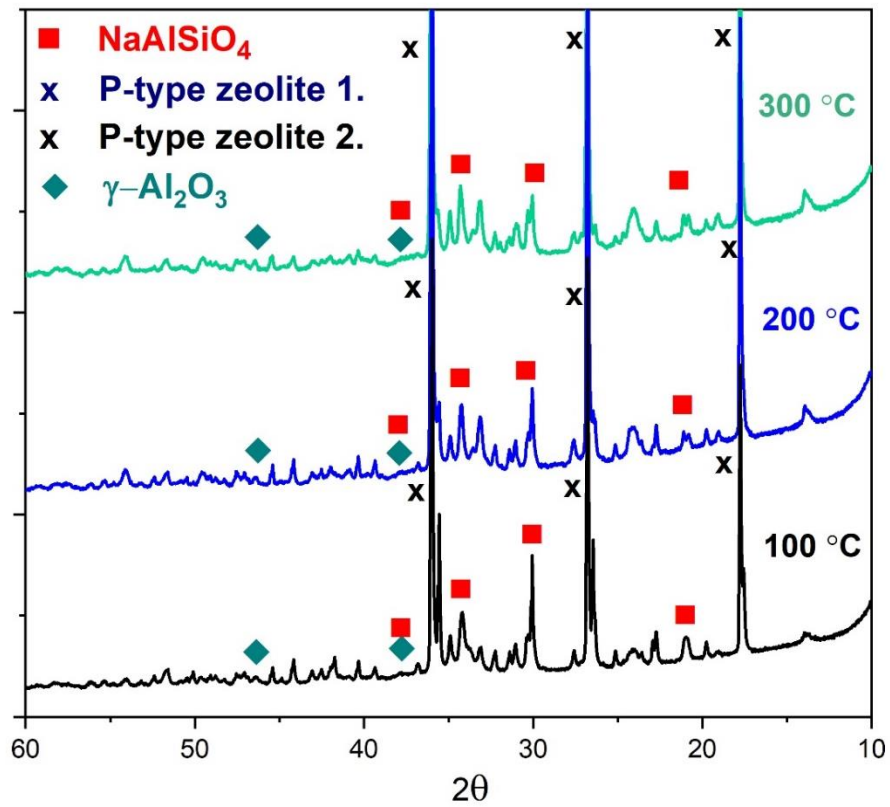


Figure 5: The X-ray powder diffraction spectra of samples containing 33% red mud, heat treated on 100 °C, 200 °C and 300 °C

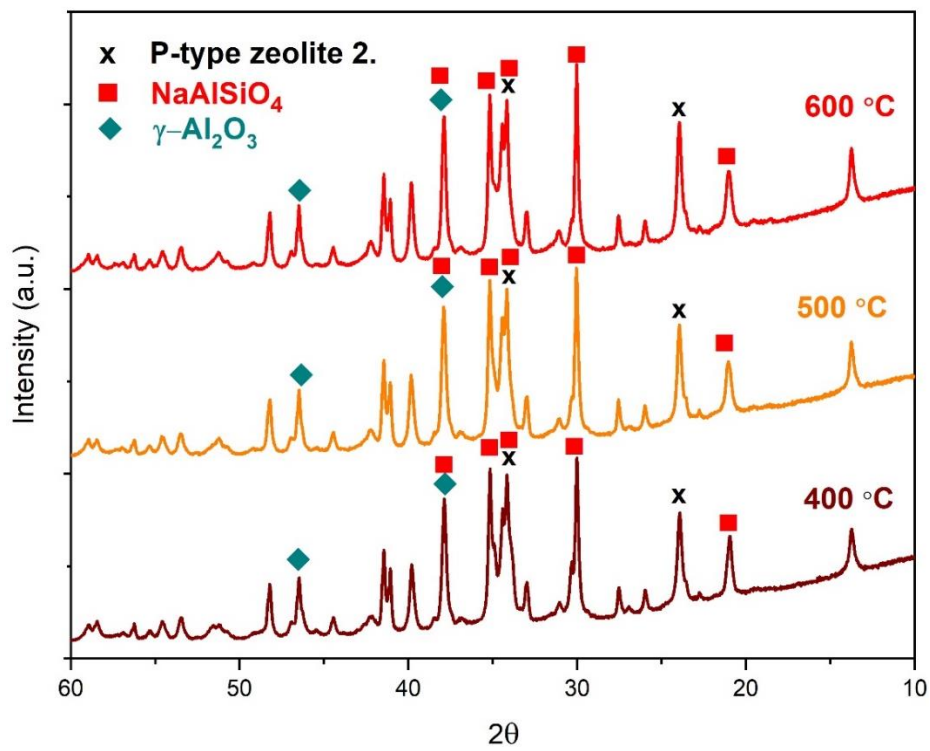


Figure 6: The X-ray powder diffraction spectra of samples containing 33% red mud, heat treated on 400 °C, 500 °C and 600 °C

## III. 2. Characterization of geopolymers

### III. 2.1 Inductively coupled plasma mass spectrometry

To evaluate the potential application as a structural material, it was important to characterize the samples' interaction with water. This was done by using inductively coupled plasma mass spectrometry (ICP-MS) technique to analyse the aqueous filtrate of samples heat treated on 600 °C. The report can be seen on Table 3., where  $m$  is the gradient of the calibration linear and n.d. means that either the values are comparable to the background, or the measured intensities have high deviation (SD). In the case of silicon, the measurement values are indicative only, due the significant memory effect. The origin is that both the atomizer and the torch of the device is made out of quartz.

Table 3.: The analytical report of the ICP-MS measurement on the filtrates of the solubility measurement of samples heat treated on 600 °C

Element	Monitored isotope	m (cps dm <sup>3</sup> µg <sup>-1</sup> )	r <sup>2</sup>	Mintaazonosító	
				Red mud sample	Synthetic sample
				concentration (mg/dm <sup>3</sup> ) ± SD	
Na	23	2380	0,9988	5636 ± 22	5261 ± 37
Al	27	508	0,9990	462 ± 3	151 ± 2
Mg	24	1·10 <sup>6</sup>	0,9993	<0,1	<0,1
Si	28	7689	0,9993	<1,0	<1,0
K	39	956	0,9997	3,20 ± 0,02	2,03 ± 0,06
Ca	44	437	0,9997	<1,0	<1,0
Sc	45	656	0,9995	<1,0	<1,0
Ti	48	6567	0,9991	<0,1	<0,1
V	51	22182	0,9983	1,93 ± 0,03	n.d.
Cr	52	34523	0,9994	0,74 ± 0,02	n.d.
Mn	55	16375	0,9999	<0,1	<0,1
Fe	56	24712	0,9956	n.d.	n.d.
Ni	58	32922	0,9999	<0,1	<0,1
Co	59	60437	0,9999	<0,5	<0,5
Cu	63	40678	0,9999	<0,3	<0,3
As	75	2919	0,9999	0,24 ± 0,02	n.d.
Rb	85	14409	0,9999	<0,3	<0,3
Sr	88	19450	0,9999	<0,3	<0,3
Mo	98	46792	0,9997	<0,5	<0,5
Cd	111	13505	0,9999	<0,1	<0,1
Sn	120	54537	0,9999	<0,5	<0,5
Sb	121	27577	0,9991	<1,0	<1
La	139	18468	0,9999	<0,1	<0,1
Ce	140	25655	0,9992	<0,1	<0,1
Gd	157	7620	0,9999	<0,1	<0,1

The high sodium ion presence is likely due to the NaOH solution, we used to dissolve the materials. The relatively high aluminium ion concentration supports the theory that the aluminium ions, instead of building the geopolymer network, remain in a water soluble form. This is supported by the results of the solubility.

### III. 2.2. Solubility

To evaluate the potential application as a structural material, it was important to characterize the samples' interaction with water. The results can be seen in Figure 12.

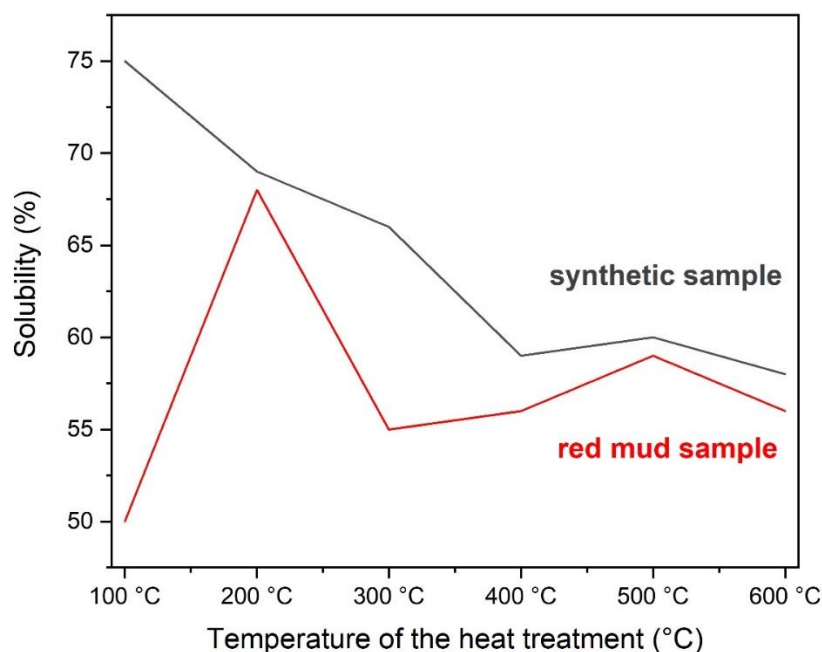


Figure 12. The solubility of synthetic and red mud samples treated on different temperatures in distilled water medium

According to the graph, a correlation can be observed between the final heat treatment temperature and the solubility in the case of the synthetic samples. In that case, there is a decreasing tendency, with respect to the growing temperature of the heat treatment. The red mud sample's values indicate that, the structure of the sample reacts differently to the temperature of the heat treatment, regarding the interaction with water. The only common change is the decrease of solubility between the 500 °C and 600 °C treated samples. This likely caused by the further building of the geopolymeric phase. The data shows higher than 50% solubility in all cases, which would be unacceptable in case of a structural material. It also shows, that the 3D geopolymeric network remains incomplete, even on 600 °C. The literature and the previous base experiments in the Sol-gel Laboratory show, that if the network is



completed, the sample shouldn't be soluble in aqueous medium. On the other hand, it can also be seen, that the solubility is enhanced by the introduction of red mud in our samples.

### III. 2.3. Thermoanalytics

To better understand the nature of the phase transformation seen on the X-ray diffractograms, synthetic and red mud samples were investigated using thermoanalytical techniques. The Figure 7 represents the thermogravimetry data of the geopolymers in the function of the red mud content.

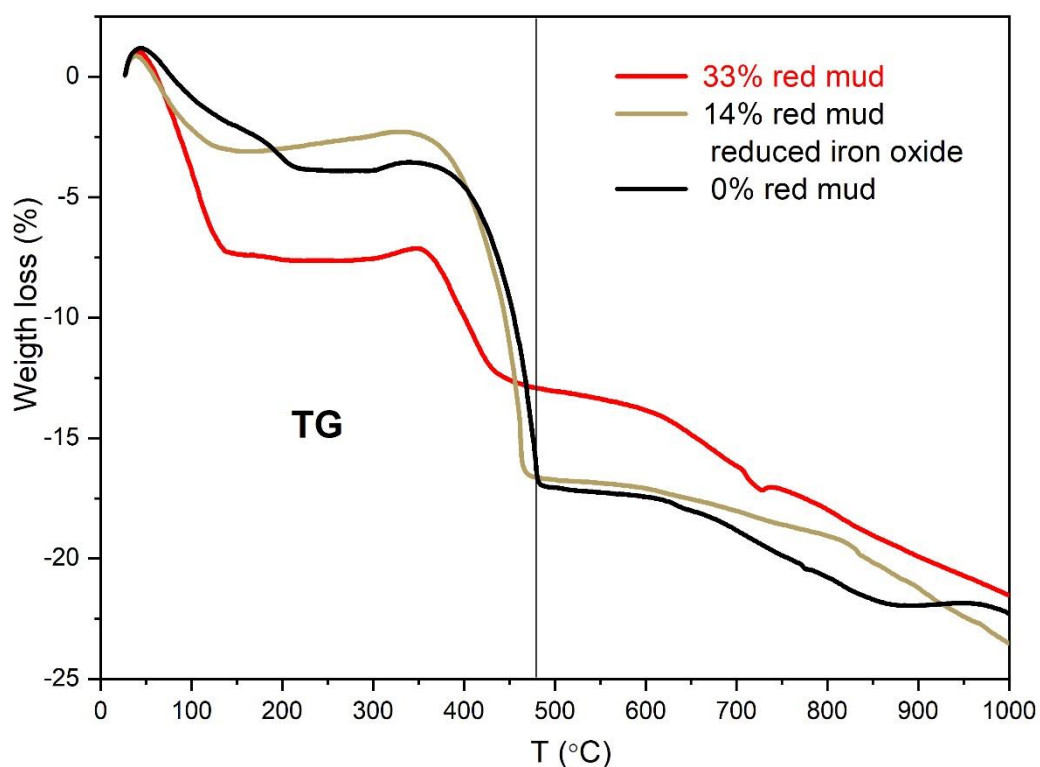


Figure 7. The results of the thermogravimetry measurements of samples heated at 80 °C vs. red mud content.

A two-step weight loss can be observed up to 480 °C. The first step is quite different for all samples, which can be attributed to remaining solvent content, after the drying process. That demonstrates, the 80 °C is insufficient for our samples, thus, we shifted the temperature of drying to 100 °C for further samples. The second step is more similar for the samples, starting from around 340 °C and finishing at 480 °C. The total weight loss of the samples during these steps were 13% for the pure synthetic, 16,5 % for the reduced iron oxide containing red mud and 17 % for the original red mud containing samples. The main part of weight loss in this range can be associated with the escape of acetate content. The weightloss continues above this

temperature, but doesn't finish at the end of the measurement in the samples of various red mud content (Fig. 7). On the DTA curves there is an exothermic peak at 460-480 °C (Fig. 8). The exothermic peak in this range can generally be connected to a crystalline phase transformation. According to the literature, this should be the formation of  $\gamma$ -aluminium oxide [47]. This crystalline process would destroy the geopolymeric structure, thus the heat treatments at higher than 600 °C should be avoided.

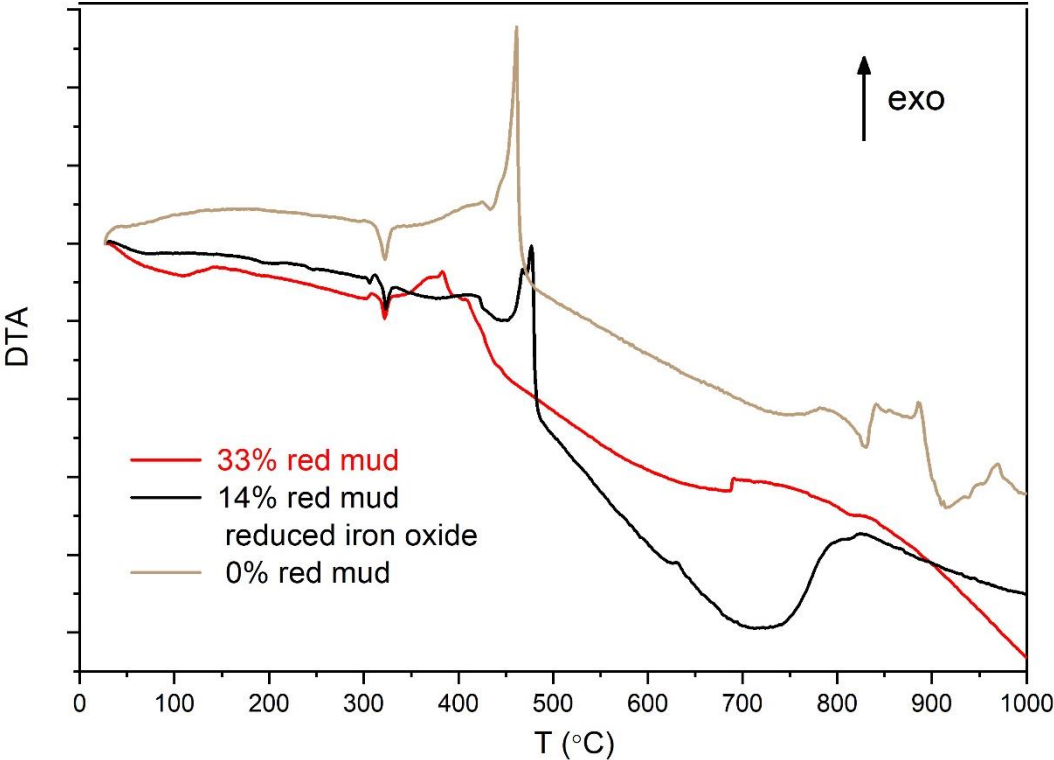


Figure.8. The results of the DTA measurements of samples heated at 80 °C vs. red mud content.

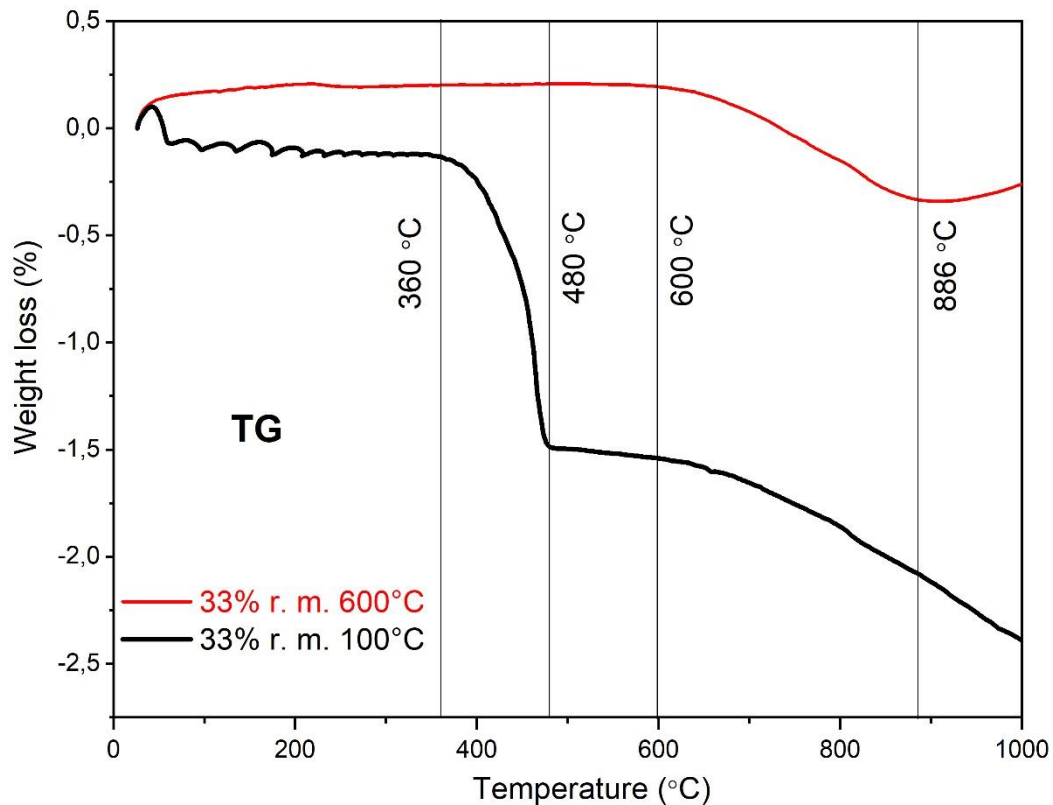


Figure 9. TG curves of samples containing 33% red mud, heat treated on 100 °C and 600 °C

The thermoanalytical investigation in the function of temperature of the heat treatment helps to understand structural changes (Fig. 9, 10). On the TG curve of the 100 °C sample, a weight loss of 15 % can be perceived between 360 °C and 480°C. That can be fitted to the escape of acetate content (TG) and the phase transformation (DTA) of the first zeolite phase. A continuous weightloss can be observed from 600 °C, in the sample heated at 100 °C (Fig. 9). DTA proves again the formation of  $\gamma$ -aluminium oxide in the sample heated at 100 °C (Fig. 10). The weight loss is finished at around 900 °C in the sample heated at 600 °C, and the exothermic peak at around 460-480 °C is disappeared on DTA curve owing to the heat treatment at 600 °C. Regarding these results, the ideal temperature of the final heat treatment is 500-600 °C. Below this temperature the structural changes are not finished yet, above that the 3D aluminosilicate network will be destroyed.

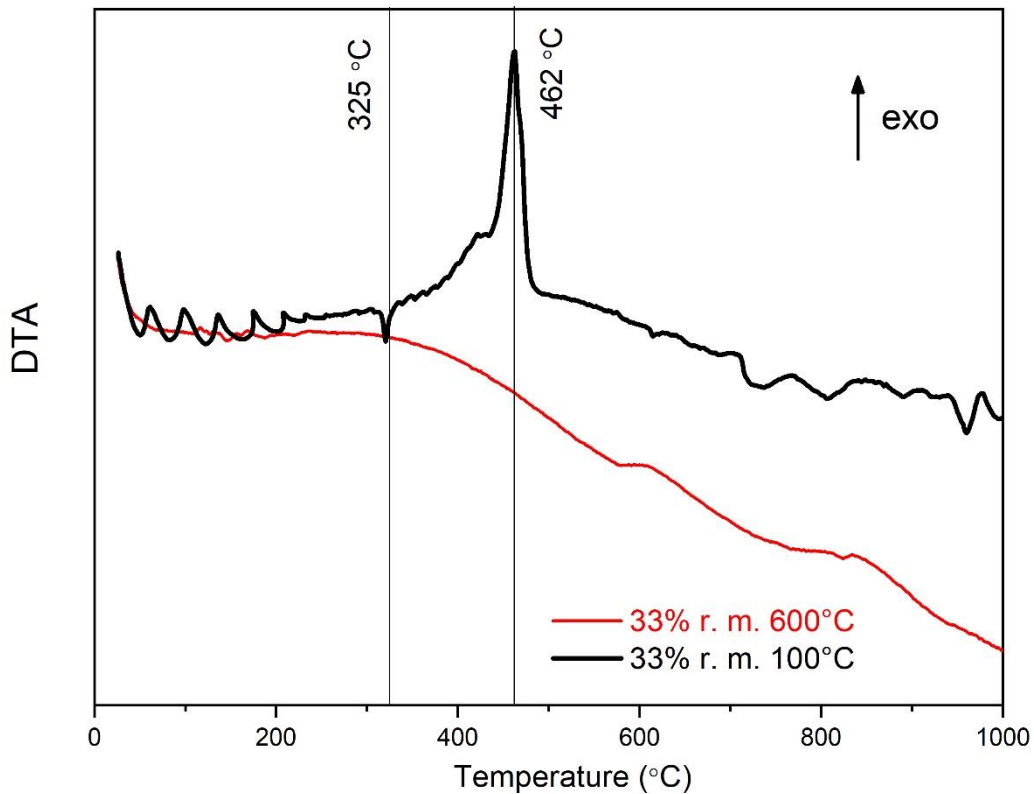


Figure 10. DTA curves of samples containing 33% red mud, heated on 100 °C and 600 °C

### III. 2.1. Compressive strength

I have also characterized the macroscopic properties of the geopolymer samples. A conspicuous property was the change of the compressive strength with respect to the temperature of final heat treatment. The compressive measurements were carried out by means of MTS (Material Testing System 810) technique. The compressive strength was investigated on both synthetic, and red mud containing samples. The mechanical characteristics of the samples heat treated at lower temperature are much different than from the ones treated at higher temperatures. The results of the synthetic samples treated on 100-300 °C can be seen in Figure 11.

These curves show a high peak, and then a gradual, but not monotone decrease in the function of load. The sharper peak means a brittle fracture process at the maximum force applied on the sample, which force is defined as the hardness of the material. On the other hand, after a steeper decrease vs. load, the curve continues to incline more gradually. The dual behaviour implies the presence of at least one brittle and a tough material phases in the samples. Comparing the curves, it can be seen that by increasing the heat treatment temperature, the maximum load of the curve becomes lower, and the first, brittle fractures's peak becomes wider, and the incline is less steep. As the heat treatment's temperature grows, the geopolymeric network should

become structured, but it isn't completed in these samples. The full 3-D structure cannot be decomposed, thus, as a polymer, it might be able to prevent the material's structural failure due to the brittle fracture.

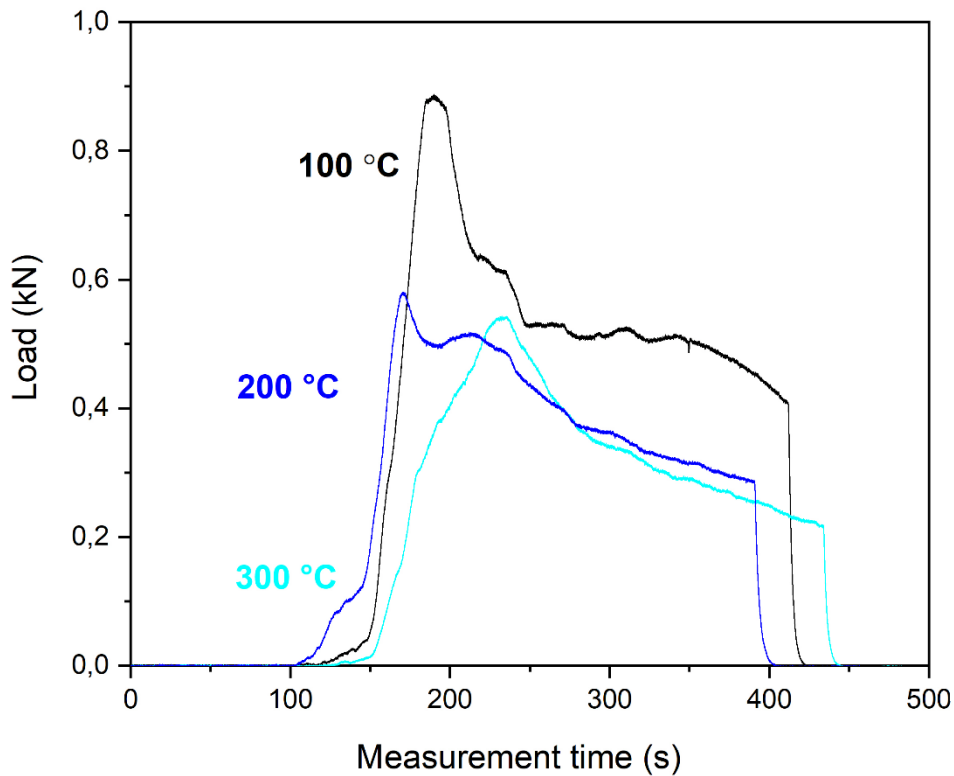


Figure 11.: The load vs. time curves of the MTS compressive strength measurement of the synthetic samples heat treated at 100-300 °C

The measurement results of the synthetic samples treated on 400-600 °C can be seen in Figure 12. The difference from the lower heat treatments is the lack of the peak at the beginning of the measurement, and show an increase of the compressive strength by the passing of time. This shows, that with the escape of the acetate content and/or the phase transformation between 300 °C and 400 °C and the brittle phase disappears. As the structure is compressed, it becomes more and more solid until a yield point. This maximum load becomes lower, if the treatment temperature is higher. That indicates, a phase transformation, beginning above 400 °C, gradually weakens the structure. The phase transformation may be a formation of zeolite-like and/or aluminum oxide crystalline phase. On the other hand the yield point of the 400 °C sample is the highest among our synthetic samples.

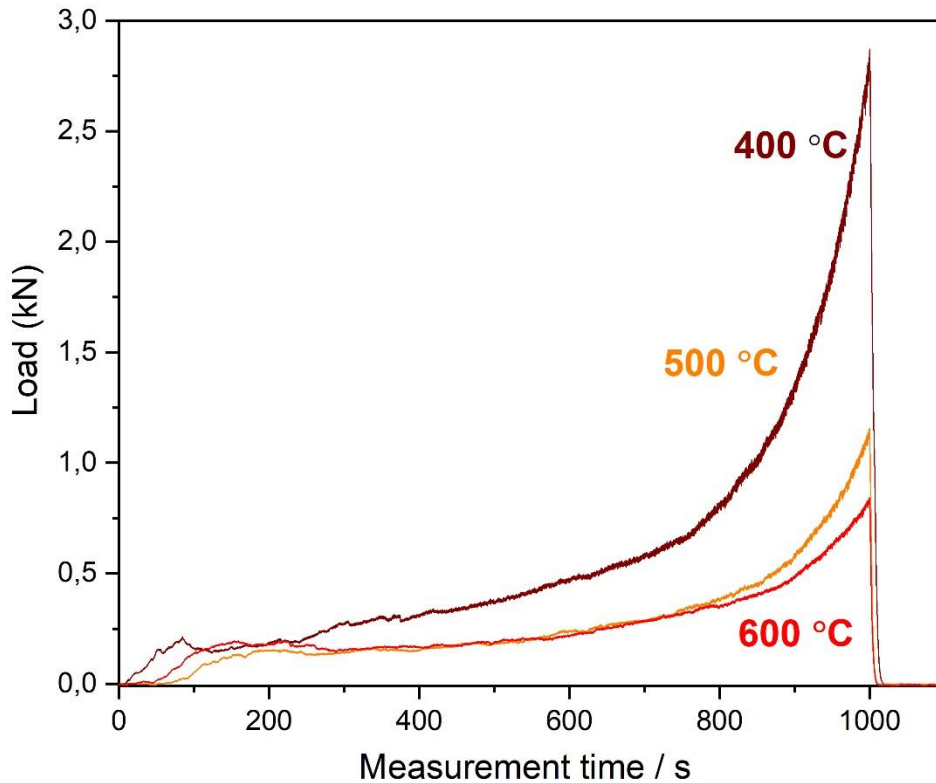


Figure 12 : The load vs. time curves of the MTS compressive strength measurement of the synthetic samples heat treated 400-600 °C

At the measurement of the red mud containing samples, identical tendencies can be observed as in the synthetic samples (Fig. 13, 14). Although, the effect of the heat treatment temperature is similar, the highest load values of the starting peaks are higher than in the synthetic samples. The peak of the brittle fracture can be seen again at lower temperatures, although at 300 °C it already displays strong properties of tough fracture. At higher temperatures, the similarity stays, with difference of the shape on the 400 °C curve. This shape can be attributed to the low pressure mode of the device, we operated on.

The maximum load in the case of most samples was between 0,48 and 2,9 kN, which equal to maximum compressive stresses ranging from 1,3 and to 9,5 MPa (See on Table 4.). Meanwhile in the case of the 500 °C and the 400 °C samples it was much higher, resulting in compressive strength comparable to cement. The maximum compressive stress of the samples with final heat treatment at 400 °C is 24 MPa, the typical compressive strength of cement is between 15 and 33 MPa.

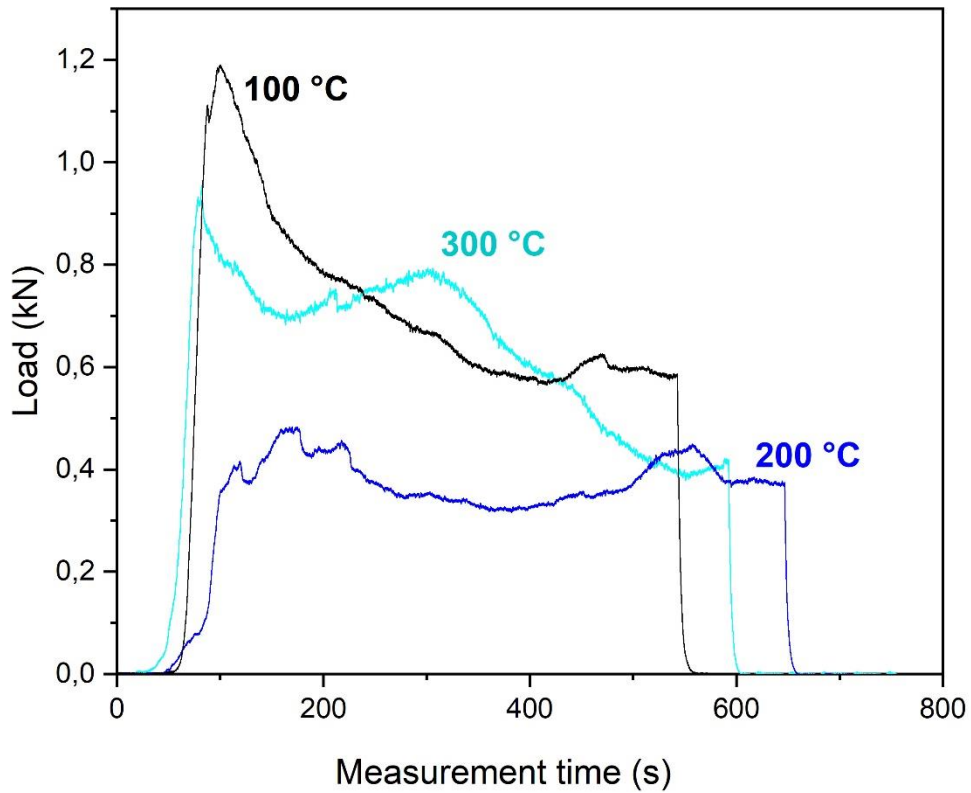


Figure 13. The load vs. time curves of the MTS compressive strength measurement of the red mud samples heat treated at 100-300 °C

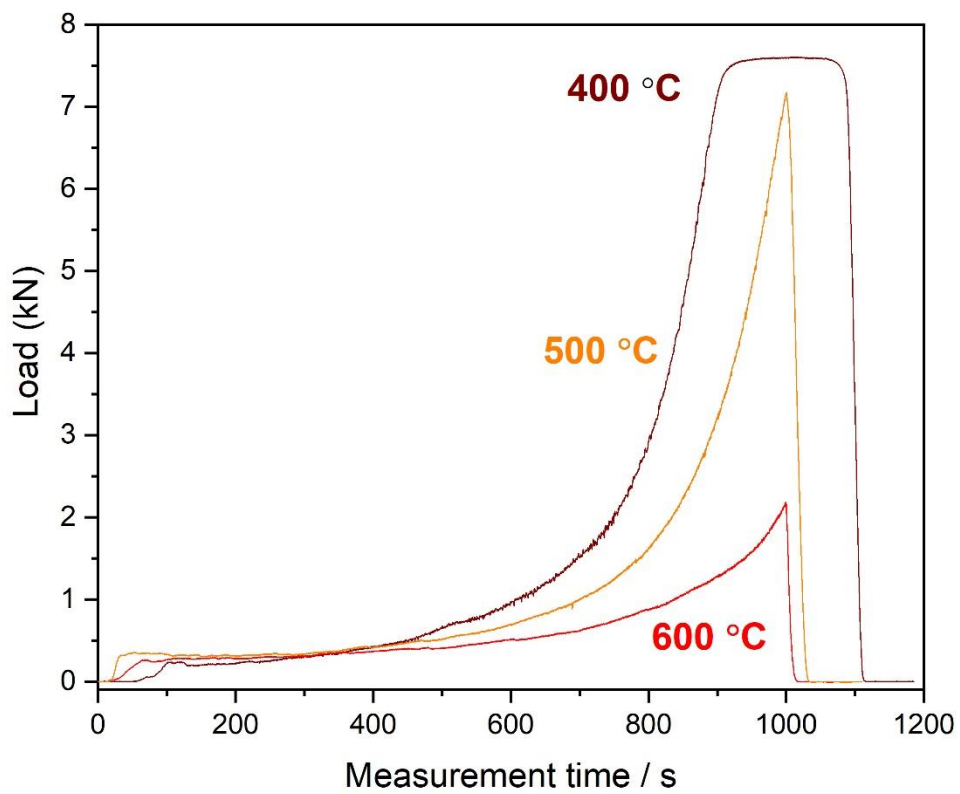


Figure 14. The load vs. time curves of the MTS compressive strength measurement of the red mud samples heat treated at 400-600 °C

Table 4. The measured maximum load and calculated hardness values of the samples with different heat treatment

Heat treatment	Synthetic samples		Red mud samples	
	Max. load (kN)	Hardness (kPa)	Max. load (kN)	Hardness (MPa)
100 °C	0,89	2,826	1,18	3,78
200 °C	0,58	1,835	0,48	1,53
300 °C	0,54	1,729	1,01	3,20
400 °C	2,87	9,140	7,59	24,16
500 °C	1,16	3,680	7,17	22,83
600 °C	0,84	2,657	2,17	6,92



## SUMMARY

One of the goals of the present research was to create geopolymers with good mechanical properties. The other one was the recycling of the industrial waste materials with respect of the environmentally friendly purpose. The very dangerous, toxic red mud as mine waste was selected for recuperation. Regarding the requirement of low energy consumption, the sol-gel method was applied to produce the geopolymers. Our starting materials were red mud, red mud with reduced iron oxide, aluminium diacetate, and sodium metasilicate.

The preparation from synthetic compounds resulted in a special nanocomposite structure due to the special molar ratio (3:1) of Al/Si. The published Si/Al molar ratios are between 1 and 5. The  $^{27}\text{Al}$  MAS NMR spectroscopy verified a nanocomposite structure in the pure synthetic geopolymers. Above 300 °C a considerable structure change occurs. "P-type zeolite I" crystalline phase is strongly dominant in the sample treated between 100 and 300 °C. Above 300 °C, this phase disappears and an other P-type zeolite and  $\text{NaAlSiO}_4$  crystalline phase develop doped some  $\gamma\text{-Al}_2\text{O}_3$  crystallites. The crystalline phases of the samples prepared with red mud are very similar to the synthetic geopolymers. The worth mentioning difference from the synthetic geopolymers is the appearance of calcium aluminum silicate.

TA measurements proved the ideal temperature of the final heat treatment is 500-600 °C. Below this temperature the structural changes are not finished yet, above that the 3D aluminosilicate network will be destroyed.

The geopolymer samples were characterized by water solubility. The ~50 % water solubility of samples must be improved. The other characteristic parameter is the compressive strength. The MTS measurements indicate that the presence of at least one brittle and a tough material phases in the synthetic and red mud containing geopolymers treated at 100-300 °C. The brittle phase disappears above 300 °C in both types of materials. The red mud content improves the mechanical properties verified by MTS experiments. The strength, by which the red mud containing samples heat treated at 400 °C can be characterized is 25 MPa, the typical compressive strength of cement is between 15 and 33 MPa.

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# NYILATKOZAT

**Név: Kóth János**

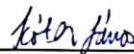
**ELTE Természettudományi kar, szask Anyagtudomány MSc**

**NEPTUN azonosító: a4gm55**

**Diplomamunka címe: Geopolymers – in environmentally friendly aspects**

A **diplomamunka** szerzőjeként fegyelmi felelősségem tudatában kijelentem, hogy a dolgozatom önálló szellemi alkotásom, abban a hivatkozások és idézések standard szabályait következetesen alkalmaztam, mások által írt részeket a megfelelő idézés nélkül nem használtam fel.

Budapest, 2022.06.01



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**a hallgató aláírása**

