

## Application of chemical treated illite clay for development of ceramics products

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**Abstract.** The chemically treatment by alkali solutions of illite clay, so-called geopolymer method, were studied to show the impact on changes of structure and crystalline phases composition of treated not dehydroxylated illite Quarternary clay, as well as ceramic properties and compressive strength of sintered respective ceramic samples. The degree of activating process were followed by FTIR-spectra, X-ray diffraction and differential thermal analysis. The low temperature ceramic product was achieved by sintering of alkali solution (KOH or NaOH 1M, 3M, 4M and 6M) activated clay samples in temperature range from 100<sup>0</sup>C to 700<sup>0</sup>C . Sintered ceramic samples were characterized by compressive strength, total porosity, bulk density and shrinkage.

It is shown that treatment of the illite Quarternary clay by KOH changes illite structure, but not destroyed. Main changes could be connected with changes of O-Al-OH grouping where O is associated with neighbour Si- layer That results into lowering of sintering temperature and development of amorphous (glassy) phase of sintered at 600-700 <sup>0</sup>C ceramic samples together with growing of total porosity. Consolidated at 600<sup>0</sup>C ceramic samples have the compressive strength ranged from 16-23 N.mm<sup>2</sup>. These values increases with growing of concentration of used alkali solution as well as with temperature for NaOH treated samples and is comparable with compressive strength for the respective ceramic products sintered at 900 <sup>0</sup>C.

### 1. Introduction

The ability to attain an increased compressive strength of aluminosilicate materials by proper mix development with activating alkali solution is well documented [e.g. 1-3]. One of more investigated solid aluminosilicate under highly alkaline conditions is the 1:1 layer lattice aluminosilicate mineral – kaolinite [2]. It is determined that to the attainment of a final strength at ambient temperatures of an aluminosilicate inorganic polymer it is required the presence of an X-ray amorphous network of aluminium and silicon atoms solely in tetrahedral coordination with oxygen. The correlation between increases of the silicon concentration in the activating solution of geopolymers and increases in the compressive strength is related to increase in densification of material at temperatures ranging from 600 to 900<sup>0</sup>C [1,4]. Despite similar composition of all geopolymers, the onset temperature of densification is observed to be higher in all K-geopolymers compared to the NaK- and Na- specimens of analogous Si/Al ratio.

Although the mainly used in the preparation of geopolymers is 1:1 layer lattice aluminosilicates, it is of interest also 2:1 minerals, e.g., 2:1 analogue of kaolinite – pyrophyllite with unit structure Al<sub>2</sub>AlSi<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub>, in which the octahedral Al-O sheet is enclosed above and below by two tetrahedral Si-O sheets to form a repeating unit [5]. Attempts to produce fully reacted aluminosilicate geopolymers from the crystalline 2:1 lattice mineral, pyrophyllite, was unsuccessful. It was suggested that inability to form viable geopolymers may be due to the retention of the crystalline 2:1 layer structure in



pyrophyllite. According to the authors [5] the enclosed Al-O sheet by the upper and lower Si-O sheets is protected from alkaline attack to form a soluble aluminate species. It is shown that disruption of the crystalline 2:1 layer lattice by severe mechanochemical ball- or vibro-milling processing enables geopolymeric materials which attain reasonable hardness and strength at 60°C. These materials were not fully X-ray amorphous, but X-ray powders show traces of zeolitic phases..

Investigations on illite-smectite clay and its possible reactivity for geopolymers is less known.

The investigations [e.g.6] focuses on the suitability of illite/smectite clay to form a geopolymer after thermal activation between 550 and 950°C and alkaline activation. It is concluded that 2:1 clay minerals such as illite and smectite yield reactive silicate and aluminate species after calcinations. The best performance can be attained by producing fully dehydroxylated clay minerals and preventing the formation of new stable phases such as spinel.

The present study investigates the impact of alkali treatment of not dehydrated illite clay on development of low temperature ceramic products.

## 2. Experimental Procedure

The starting materials were Quaternary clay samples taken in the Laza pit (Latvia) from the 2-3m depth of the soil and KOH, NaOH pellets used for preparation of 1M, 3M, 4M 6M respective solutions for treatment of clay. In general clay deposits characterize fair carbonate and relatively high clay fraction content. SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, mol. ratio is 1.45. For the investigations intermediate composition of clayey material were used. The chemical and mineralogical compositions of this clay show the table 1.

**Table 1.** Chemical and and grading composition of the clay (wt.%)

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Ignition loss at 1000 °C
46.87	18.74	7.06	0.59	6.62	3.25	3.62	0.41	12.84
Sand fraction,			Aleurit (dust) fraction,			Clay mineral fraction		
>50µm			50-5 µm			<5µm		int.al.<2µm
1.33			8.67			90		60
Mineralogical composition of the clay fraction (wt.%)								
Illite			Chlorite			Kaolinite		
78-80			6-8			10-12		

As it is shown the clay mineral fraction (mainly) is presented by illite, chlorite and kaolinite, but aleurit fraction - by dolomite and calcite.

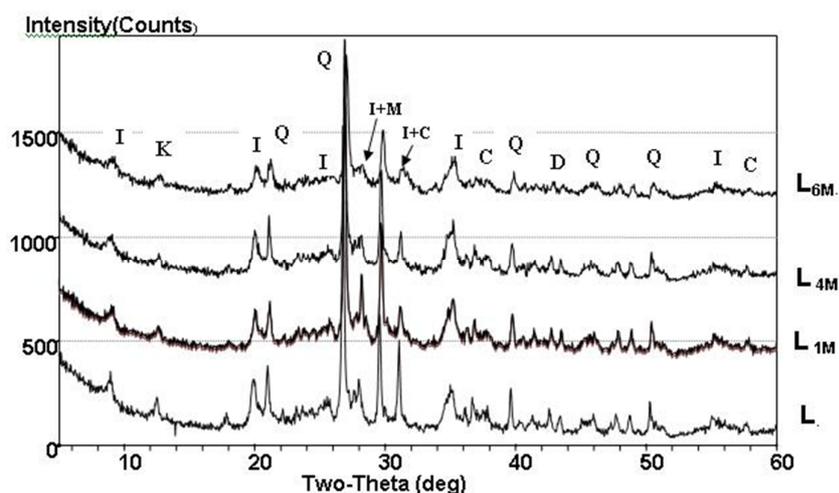
The starting raw clay were to grind and the possible undesirable hard inclusions were separated by screening (Retsch equipment AS200 sieve with aperture 1.0 mm) to obtain the clay powder for chemical activation with 1M, 3M, 4M, and 6M KOH- or NaOH solutions. The solution/solid ratio was fixed to 20% solution to clay powder yielding a good workability (plasticity) of the clay. The solution-clay mix was aged for 24h at room temperature. Thereafter treated and dried mix was investigated by IR-spectroscopy (spectrophotometer IR prestige-21FTIR-8400S) to establish possible changes of the structure and by thermal analysis using a Setaram, SETSYS Evolution -1750 model at temperature range from 20 to 1000°C and a heating rate 10°C/min in flowing technical air (200ml/min). X-ray diffraction (XRD-model Rigaku, Japan, with CuK<sub>α</sub> radiation at scanning interval from 2θ=10...60° and speed 4°/min) was used to determine the crystalline phase changes both for chemically treated clay, and sintered ceramic samples.

For investigation of ceramic properties as well as a compressive strength from each treated mix were formed cylindrical samples (Ø- 25mm,h -30mm) by using of laboratory extruder. These samples were sintered (thermal curing) in laboratory furnace (Nabertherm HT 16/17) at temperatures 100, 300, 600 and 700°C by the temperature growth rate 5-6 °/min. and the holding time at each temperature for 15 min. Investigation of some ceramic properties (total porosity, bulk density), as well as compressive strength were performed in accordance with EN. For pressure strength measurement was used Toni-

technic model 2020. Five samples were measured for each mixture from where the mean value was calculated.

### 3. Results and Discussion

Fig. 1 presents the XRD patterns of chemical treated dried clay samples. It is clearly visible reflections of illite and weakly shaped from kaolinite.

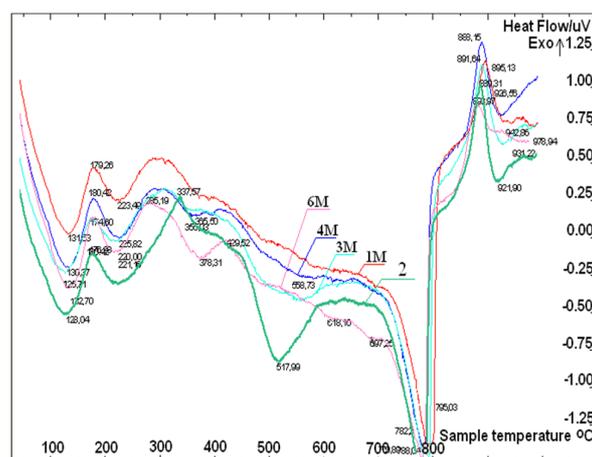


**Fig.1.** XRD patterns of untreated (L) and treated by 1M (L<sub>1M</sub>), 4M (L<sub>4M</sub>) and 6M (L<sub>6M</sub>) KOH-solution clay: **I**- illite  $K(AlFe)_2AlSi_3O_{10}(OH)_2 \cdot H_2O$ ; **K** – kaolinite  $Al_2Si_2O_5(OH)_4$ ; **Q** – quartz  $SiO_2$ ; **M** – microcline or orthoclase  $KAlSi_3O_8$ ; **C** – calcite  $CaCO_3$ ; **D** – dolomite  $CaMg(CO_3)_2$

X-ray of the starting clay and after the alkaline activation shows relative decrease of all comparable

main peaks of illite and kaolinite (at  $2\theta = 8^\circ, 12^\circ, 20^\circ$  and  $35^\circ$ ) as well as for quartz (at  $2\theta = 21^\circ, 26.5^\circ, 30.5^\circ$  and  $40^\circ$ ), calcite and dolomite. It means that the crystalline structure of clay minerals - illite and kaolinite phases is to weaken. Small changes can be observed also for quartz and carbonate containing phases.

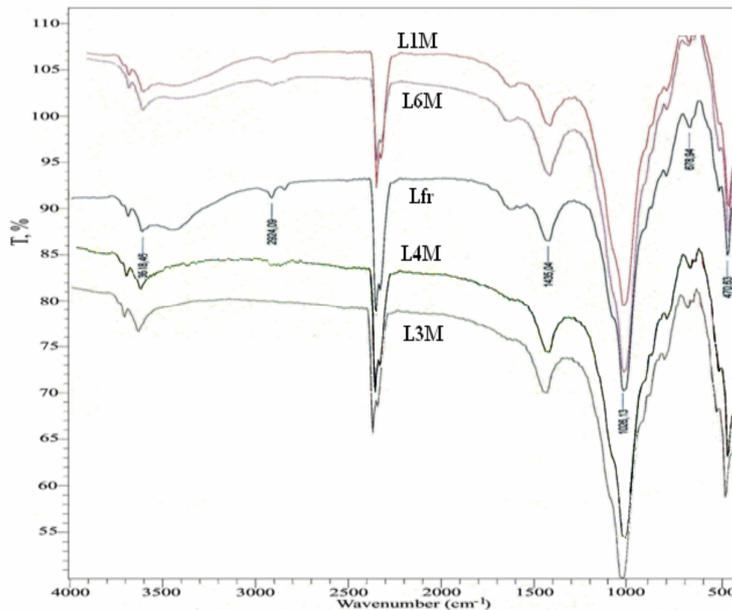
DTA curves (Fig. 2) demonstrate that for differently treated clay samples remarkable changes of curves is observed in the temperature range up to  $500^\circ C$ .



**Fig. 3.** DTA- curves for untreated clay (L) and treated with different concentration of KOH solution

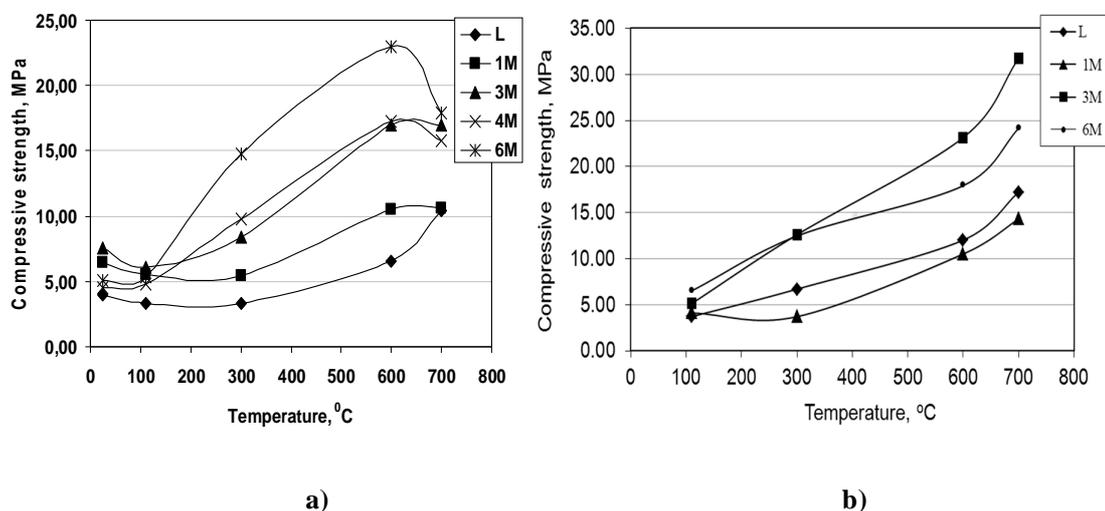
DTA curves (Fig. 2) demonstrate that for differently treated clay samples remarkable changes of curves is observed in the temperature range up to  $500^\circ C$ . This characteristic endo-peak for illite normally is connected with the structural water losing and is visible only for untreated clay. That show on the structural changes of illite after chemical treatment. It is necessary to note also that for all treated clay samples with respect to concentration of used KOH solution disappears the exo-peak at  $337^\circ C$  bounded with decomposition of organic admixtures. In a way it correlate with water link changes in illite structure for treated clay samples and weakly is shown from FTIR.

The FTIR-spectra (Fig. 4) of clay samples treated by 1M, 4M and 6M KOH solution in comparison with untreated clay ( $L_{fr}$ ) show small change in oscillations: - by OH-stretching bands at 3700 -3500  $cm^{-1}$  and by 2920  $cm^{-1}$ , and can be connected with oscillations of OH- and water link changes in illite structure, namely with O-H-OH grouping where O is associated with neighbour Si-layer.



**Fig. 4.** FTIR- spectra for untreated clay  $L_{fr}$  and treated with 1M to 6M KOH solutions

Following figures (Fig. 5a, b) illustrate the effect of chemical treatment of KOH and NaOH on compressive strength values of sintered at temperatures under 700°C ceramic samples.



**Fig. 5.** Compressive strength development of ceramic samples from treated clay (a – by KOH, b- by NaOH) in dependence on sintering temperature.

Despite of the observed relatively small structural changes for treated clay samples it is required to be noted on considerable impact on compressive strength and also on ceramic properties of sintered ceramic samples. Yet the relatively big total porosity (30-40%) slightly increased with concentration of used KOH- or NaOH solution and sintering temperature, the compressive strength for all ceramic samples from treated clay sintered by increasing temperature, growth (except of samples from KOH treated clay at 700°C) and reaches considerable values which is comparable with compressive strength for the respective ceramic products sintered at 900°C.

This fact allows authors suppose that observed grows of strength is associated with development of amorphous (gel-shaped)  $K^+$  or  $Na^+$  -containing aluminosilicate products by reactions of KOH or NaOH with clay ingredients. The greatest values of compressive strength for NaOH treated samples, in particular by 3M NaOH, show on more effective influence on destruction of clay structure than KOH.

#### 4. Conclusions

Alkaline activation with a potassium and sodium hydroxide 2:1 layer aluminosilicate – illite clay has been studied.

The study shows that alkaline activation of raw illite clay by potassium solution of different concentration at room temperature leads to the slight structural changes mainly characterized by water link changes in illite structure together with decrease of diffraction peaks of clay minerals – illite and kaolinite, as well as also quartz and carbonates containing phases. .

It is noted that despite on observed small structural changes on considerable influence on compressive strength in whole sintering temperature interval under 700 °C, as well as on ceramic properties and particularly on changes of total porosity, bulk density and total shrinkage of ceramic samples.

It is shown that increase both of sintering temperature and molar concentration of used KOH- or NaOH-solution gave rise for growth of compressive strength in whole sintering temperature interval by reaching maximum values at 600-700°C.

#### References

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