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Chemical and microbiological processing for modification of 2:1 sheet silicate structure and properties

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Topicality

Developing advanced ceramics materials, used in industrial, building and domestic products, will continue to be important and closely connected with reducing our energy consumption and our impact on the enviroment.

Paliek!

A new ceramics product can be characterised with:

- **Reduced sintering temperature**
- **Reduced thermal conducivity**
- **Optimal provision of ceramic properties**
- **Optimal provision of mechanical properties**

Acknowledgement. This work was supported by the Latvian State Research Program „Long term applications of local resources – new products and technologies (Nr.10-4/VPP-5), subproject „New ceramic products and technologies”.

The aim of the work

The aim of this work is to show impact of NaOH of different concentrations and biological impact (Pseudomonas fluorescens bacterium treatment) on illite clay in an attempt to change or “ruin” specific network-forming linkages among Si-O and Al-O units.

Paliek!

Work tasks

Nost mikrobiologiško apstr.

- To prepare the clay powder by granulation and screening.
- To activate with 1,3, 4 and 6 M NaOH solutions and with Pseudomonas fluorescens bacterium AM-PS11.
- To determinate the crystalline phase changes both for chemically and biologically treated clay mixes and sintered ceramic samples.
- To perform cylindrical clay samples forming and sintering at temperatures 100, 300, 600 and 700°C .
- To investigate and to analyse ceramic and mehanical properties.

Experimental methods

Yield of an average clay sample from 2-3m deep layer of clay

To grind and screen clay sample

Preparation of powdery samples for treatment with 1M, 3M, 4M and 6M NaOH solutions

Successive treatment of samples with NaOH solutions for 24h

Study of the treated clay: XRD, IR-spectra, DTA

Preparation and sintering of the samples in temperature range from 100°C to 700°C

Investigation of ceramic properties (total porosity, bulk density, shrinkage) as well as compressive strength

Paliek!

Experimental methods

Yield of an average clay sample from 2-3m deep layer of clay

To grind and screen clay sample

Sterilization of clay 121°C, 15min; 24h cultivation of Ps. Fluorescens

Incubation of clay suspension with culture liquid

Study of the treated clay: XRD, IR-spectra, DTA

Preparation and sintering of the samples in temperature range from 100°C to 1000°C

Investigation of ceramic properties (total porosity, bulk density, shrinkage) and flowability

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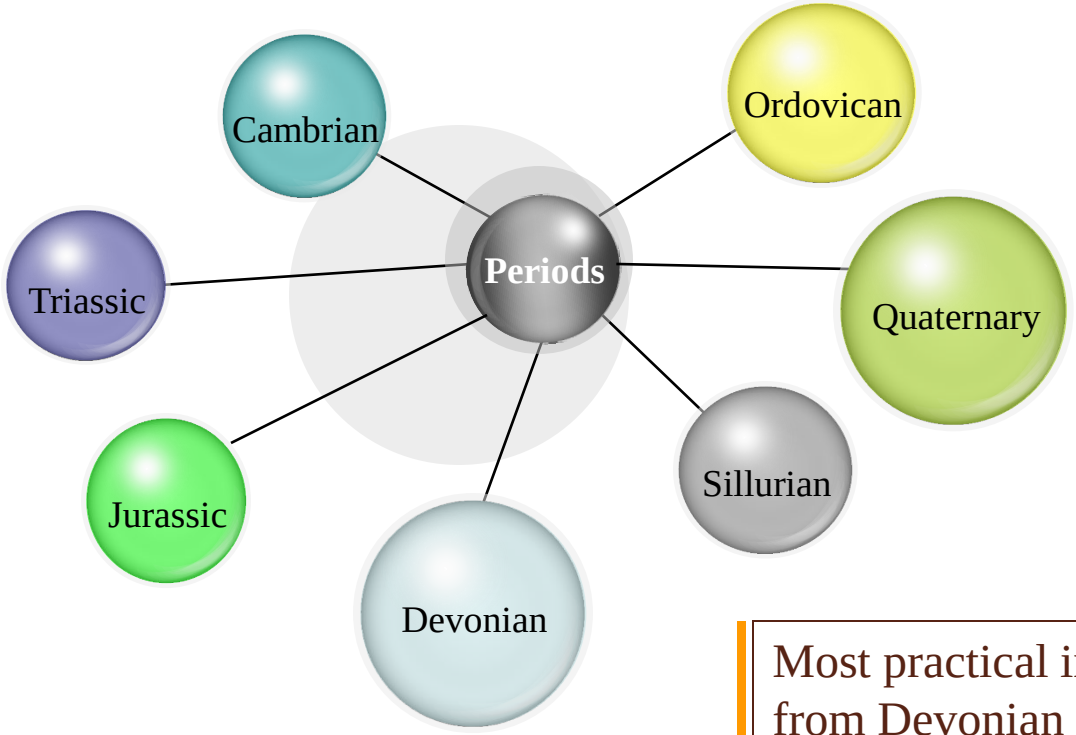
General characterization of clay sediment

Clay deposits are wide spread and most important mineral wealth in Latvia, they can be found at various stratum depths from Cambrian to Quaternary geological periods. The most widely spread clays are illites - they form 70-80% of the total volume with slight admixture of chlorites, smectites and kaolinites.

The deposits of geological periods that contains clayey rock:



Varētu noņemt! – ģeologiem tas ir labi zināms

Most practical importance is for the clay from Devonian and Quaternary periods.

Clay from Quaternary period

The creation of Quaternary sediments began 70 thousand years ago. Clayey rocks are the youngest and they cover all the territory of Latvia.

Noņemt!

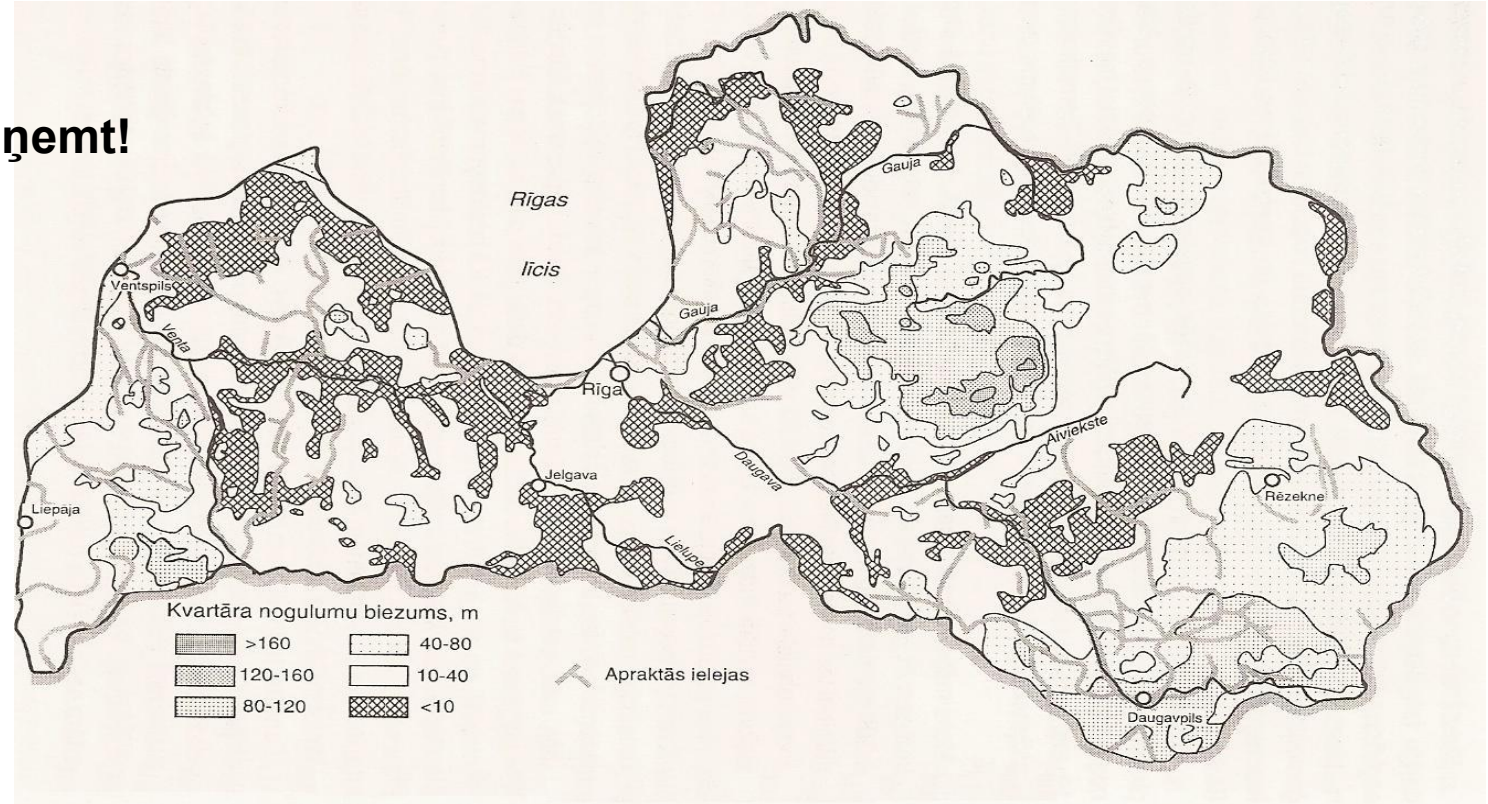
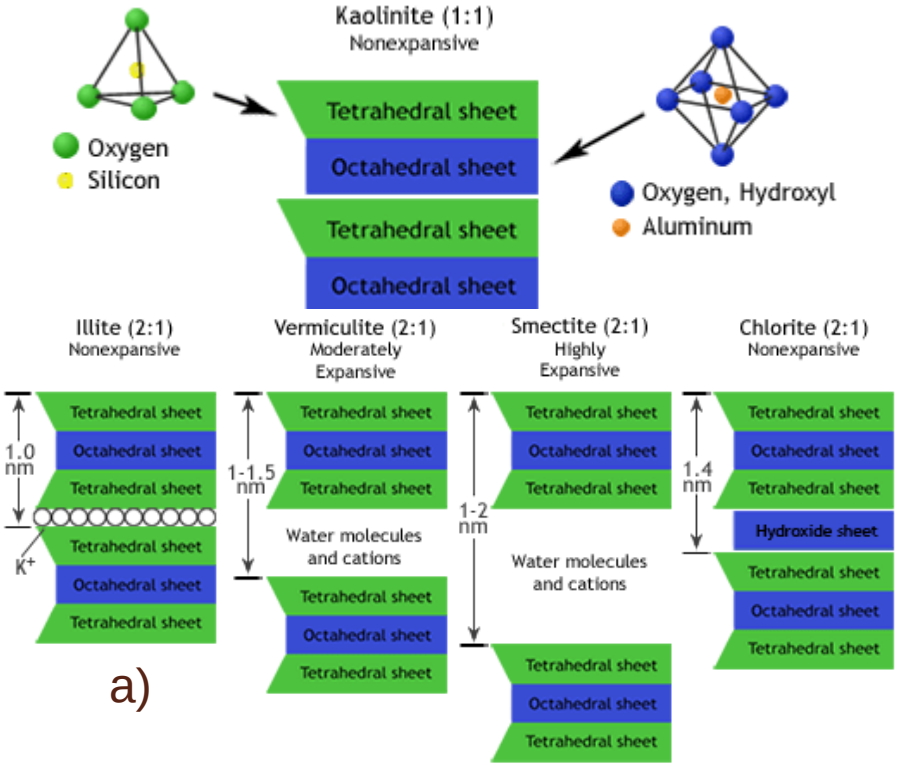


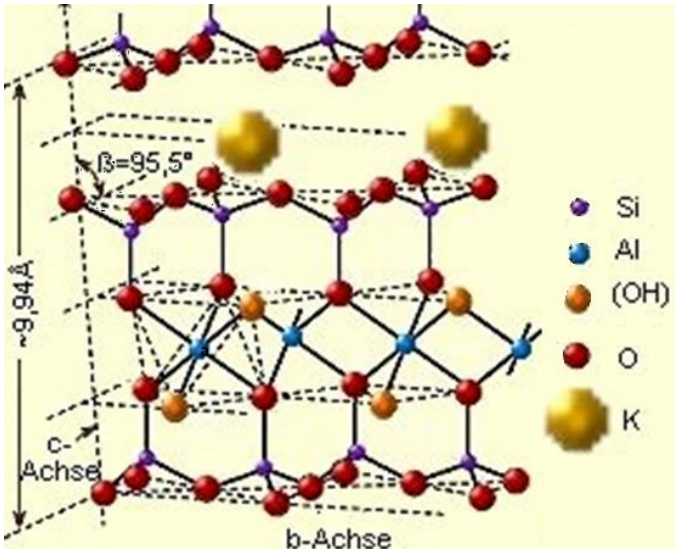
Fig.1. The thickness of Quaternary sediments according to the data of geological mapping

Structure of clay

- Clay is the sedimentary rocks, that start forming from magmatic and metamorphic rocks decomposition pruducts.
- Main groups of clays are clay's minerals - kaolinite, illite, montmorilonite.
- In structurical they are layered alumosilicates, those main structure element are repeatable tretrahedral Si-O and octaethedral Al-O sheets.



a)



b)

a) Diagrammatic representation of different clay minerals
b) Cristal lattice of illite

Paliek

Processes occurring during sintering

Traditionally clay is used for production of domestic, industrial, building products and art objects. Firing them at maximum temperatures, between the intervals of 950 -1050 ^{o}C, is a part of production process

Varētu noņemt!

The main reactions occuring by sintering

the dominating reactions taking place in clays in the interval of temperatures above 600-700 ^{o}C are as follow:

- separation structural water from illite structure:

$(K,H_3O)Al_2(OH)_2[(Si,Al)_4O_{10}].n\ H_2O \rightarrow K[AlSi_3O_8] + Al_2O_3 + SiO_2 + H_2O$

- simultaneously at 620 – 912 ^{o}C carbonates of the clay decompose:

$CaCO_3 \cdot MgCO_3 \rightarrow CaO + MgO + CO_2\uparrow$

- Fe^{3+} reduces to Fe^{2+} ; $Fe_3O_4 \rightarrow FeO + O_2\uparrow$

- forming a eutectic mixture/liquid phase – the material shrinks becomes denser and harder

Processes occurring in clay under alkaline activation

Atstāt!

The chemical activation of clay minerals/clays with alkaline hydroxides can form materials with fundamental different properties, such as a ceramic material with sufficient strength, at temperature which is less than the traditional firing temperature.

Schematic representation of the structural changes of the clay minerals under the impact of alkaline can be described with reactions:

- $(K,H_3O)Al_2(OH)_2[AlSi_3O_{10}].nH_2O + 3K^+ + 3OH^- \ (H_2O) \Rightarrow$

illite

$\Rightarrow 3\,Al(OH)_3 + 3Si(OH)_4 + 4K^+$ or $\Updownarrow$ $K_4Al_3Si_3O_{12} + n\,H_2O$

zeolite similar to ceolite

- dissolution of kaolinite and forming soluble Si-OH and Al-OH groups

a) $Al_2Si_2O_5(OH)_4 + 6OH^- + H_2O \Rightarrow 2Al(OH)_3^- + 2H_2SiO_4^{2-}$

kaolinite

b) formation of feldspathoid - hidrosodalite:

$6Al(OH)_3^- + 6H_2SiO_4^{2-} + 6Na^+ \Rightarrow Na_6Si_6Al_6O_{24} + 12\,OH^- + 12H_2O$

zeolite similar to ceolite

Processes occurring in clay under biological treatment

The biological treatment of clay minerals/clays can impact on rheology of clays.

The hypothesis of processes in clay by biological treatment:

- flowability-degradation illite clay by change water content;
- anionic and cationic exchange capacities;
- technological characteristics such as shrinkage, plasticity and sensitivity to drying;
- the chemical and physical properties and phase changes (less possible)

Noņemt!

Experimental procedure

The clay from the Laza quarry (Kurzeme district, Latvia) was taken from 2-3m depth layer.

Different concentration of NaOH solutions: 1M, 3M, 4M and 6M.

Chemical and grading composition of the Laza quarry clay

Chemical composition of the clay (wt.%)

SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	TiO_2	Na_2O	K_2O	I.O.I.*
46.87	**18.74**	6.62	3.25	7.06	0.59	0.41	3.62	12,84

*Loss on ignition

Varētu palikt!

Grading composition of the clay (wt.%)

Sand fraction > 0.05 mm	Aleurit (dust) fraction 0.05 - 0.005mm	Clay mineral fraction	
		<0.005 mm	int.all< 0.002mm
1.33	8.67	90.00	63.60

Biological treatment

- *Pseudomonas fluorescens* are Gram-negative rod shaped bacteria that inhabit soil, plants, and water surfaces;
- These bacteria are easy to culture, as they grow on minimal media and at 25-30°C and grow fairly quickly;
- Samples of *Pseudomonas fluorescens* for study are available from some companies that supply stabilized bacteria for research in samples designed to be free of contaminants.
- As these bacteria produce a lot of around production, they is very economically advantageous.

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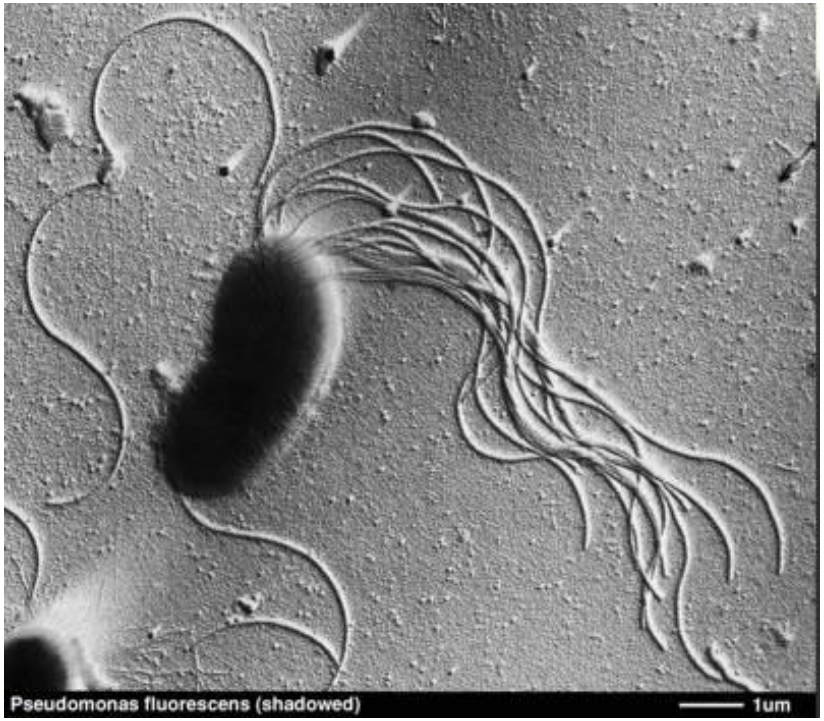
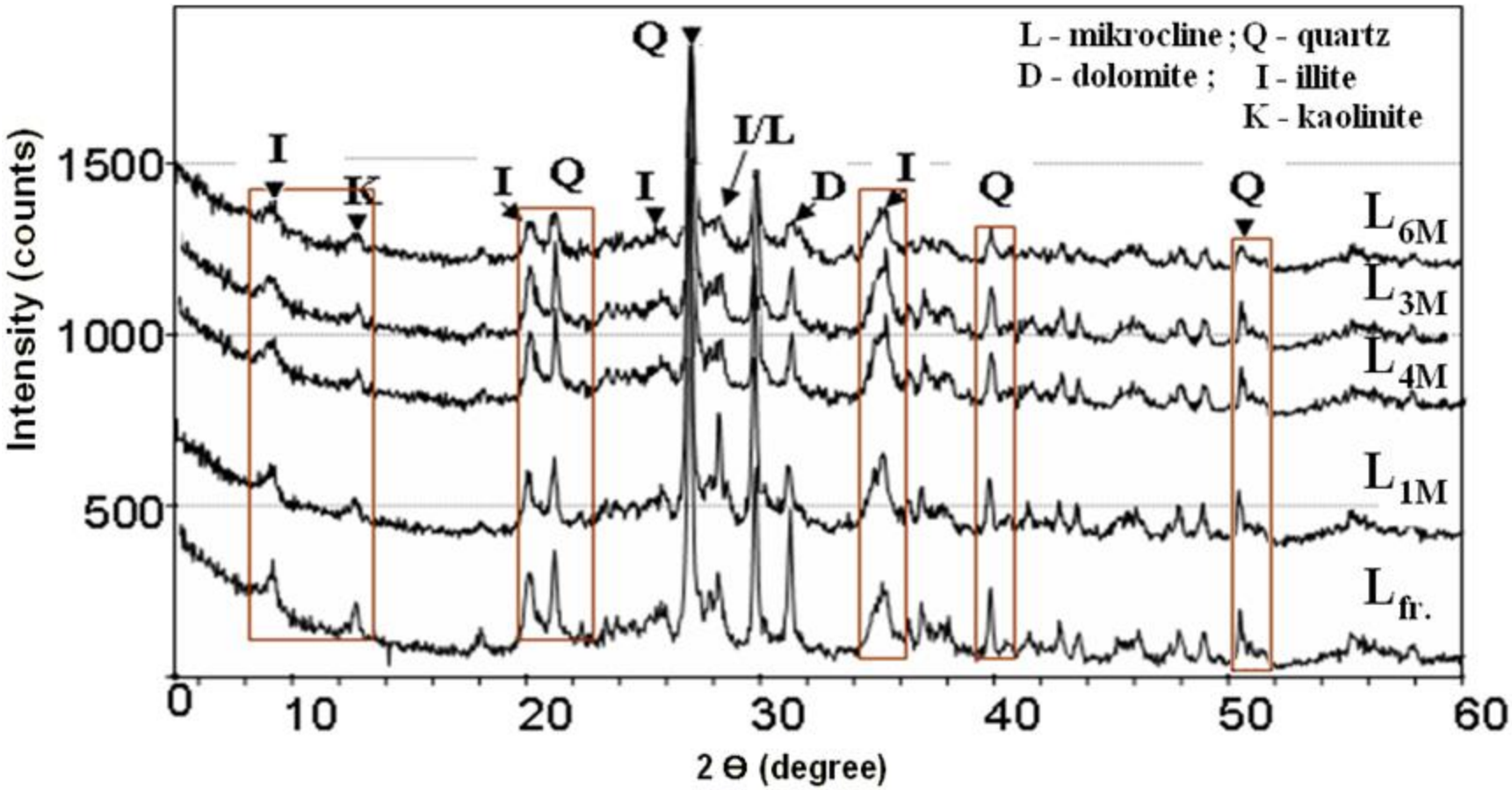


XRD



Atstāt!

Fig. 1. XRD-patterns of not treated clay Lfr. and treated with NaOH solutions

It must be noted that changes of crystalline phases intensity for raw clay $L_{fr.}$ by the microbiological treatment is not observed.

IR-spectra

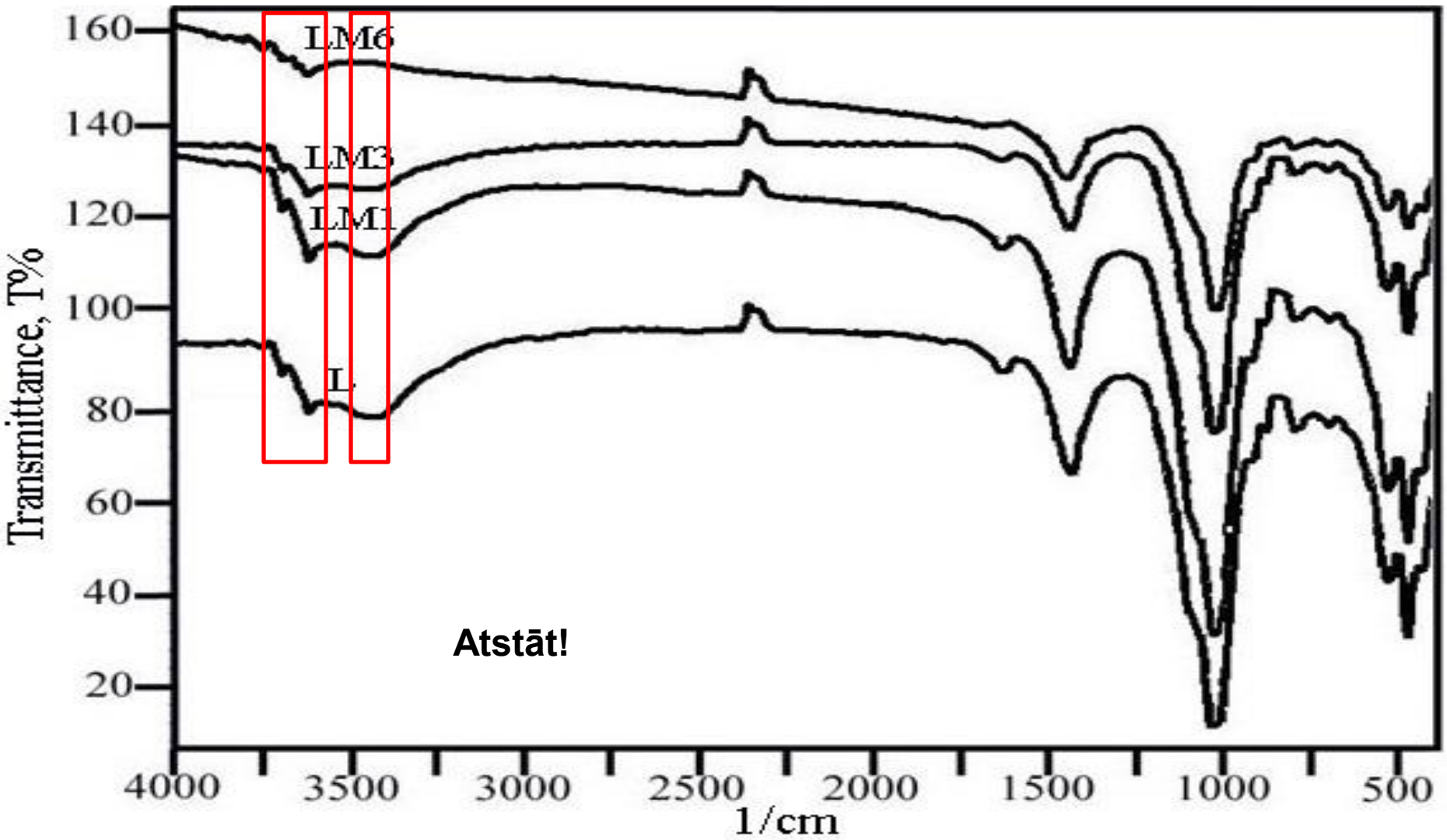


Fig. 2. IR-spectra of not treated clay L and treated with NaOH solutions

IR-spectra

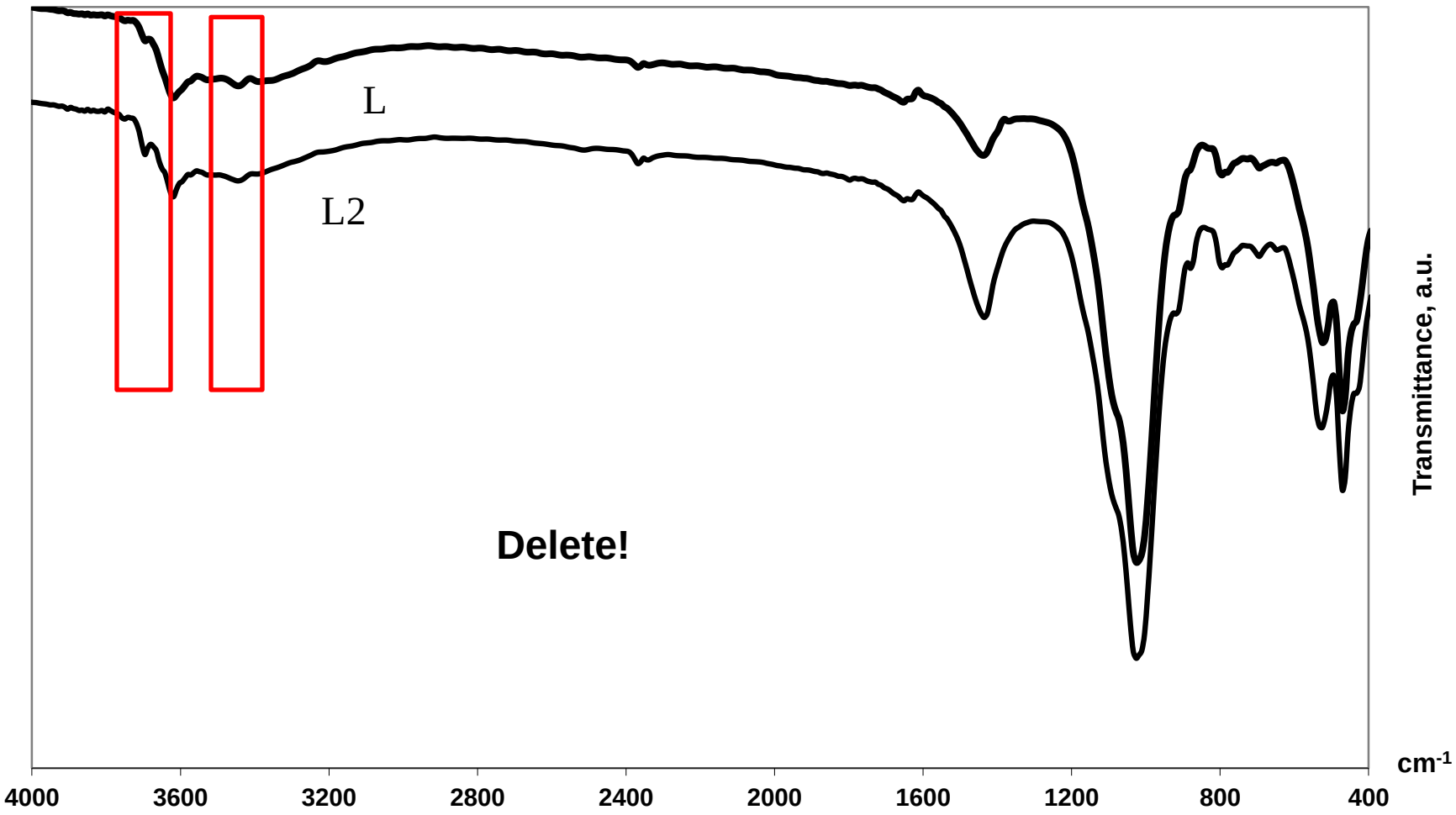


Fig. 3. IR-spectra of not treated clay L and treated by Ps. Fluorescens bacteria

DTA

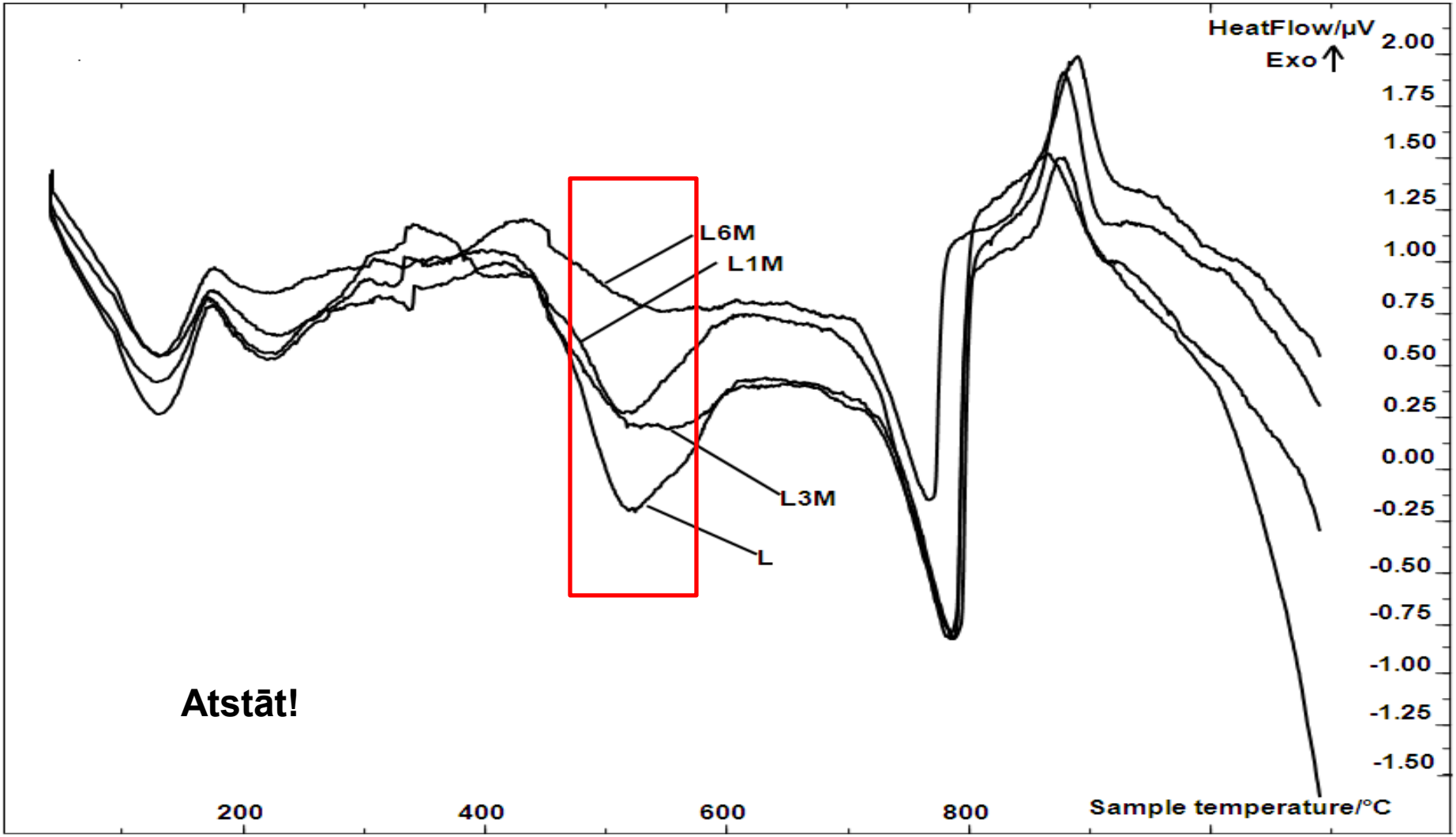


Fig. 4. DTA- curves for not treated clay **L** and treated with NaOH solutions

DTA

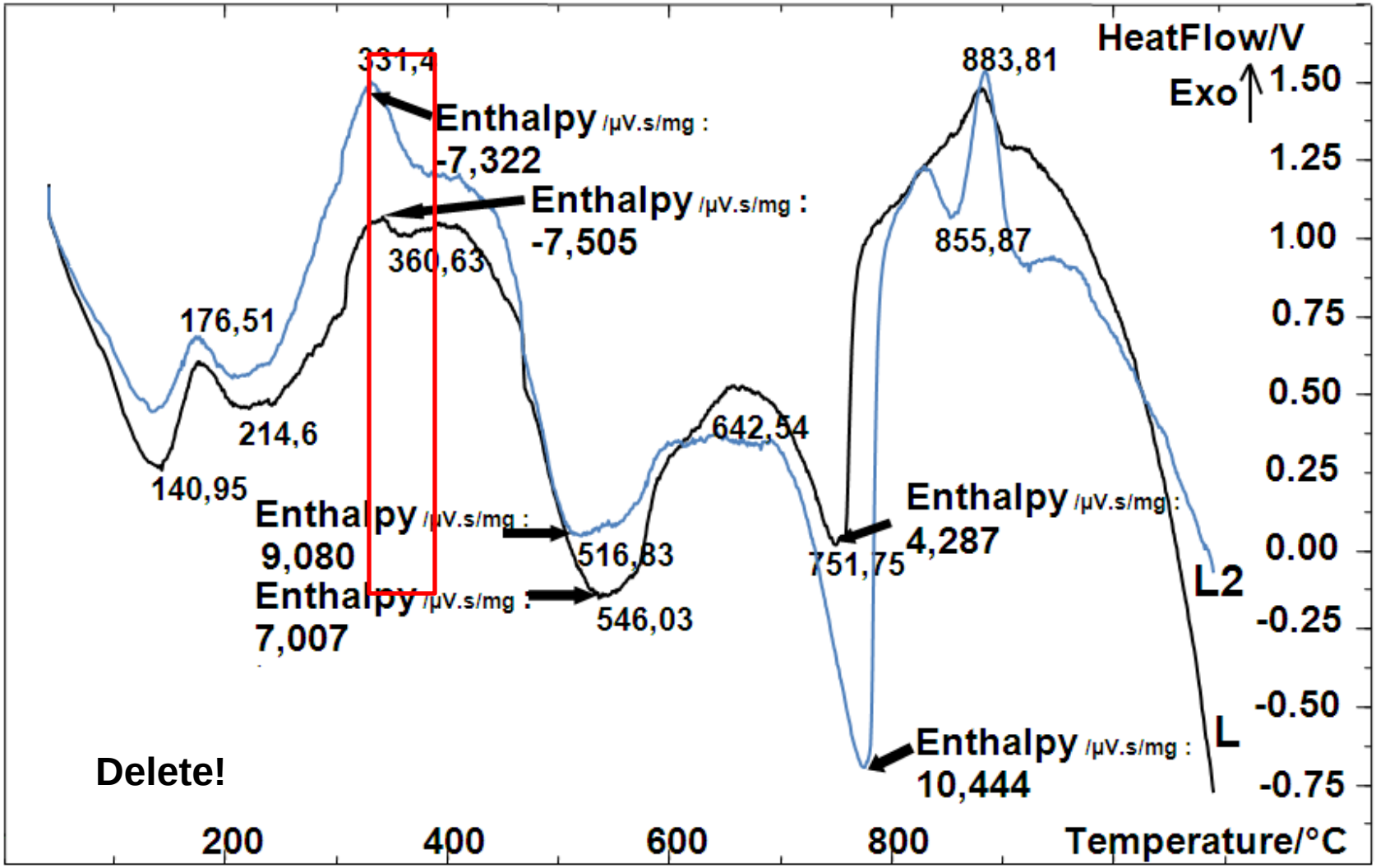


Fig. 5. DTA- curves for not treated clay **L** and treated by Ps. Fluorescens bacteria

Results and discussion

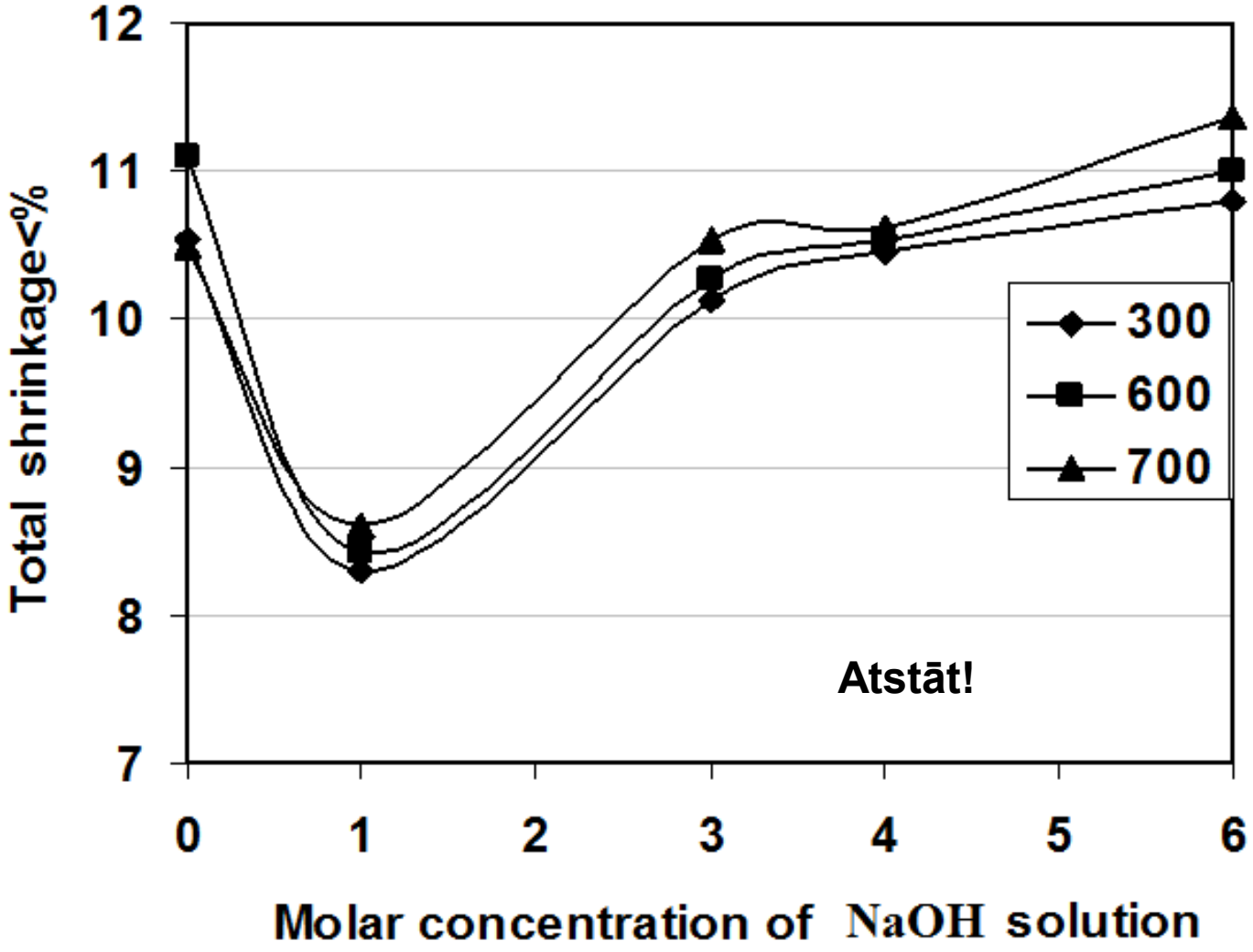


Fig. 6. Total shrinkage of ceramics samples in dependence of molar concentration of NaOH solutions.

Results and discussion

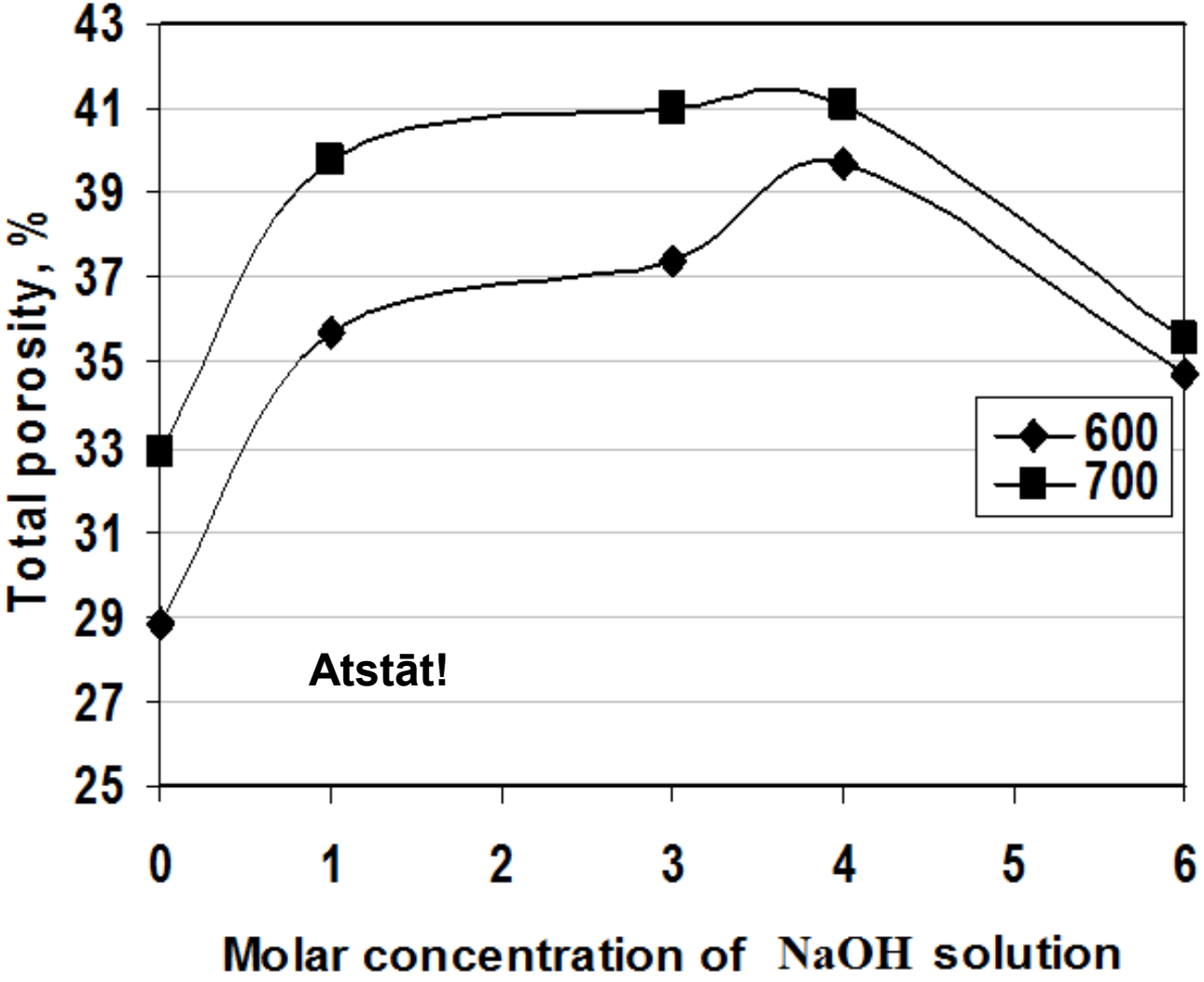


Fig. 7. Total porosity of ceramics samples in dependence of molar concentration of NaOH solutions.

Results and discussion

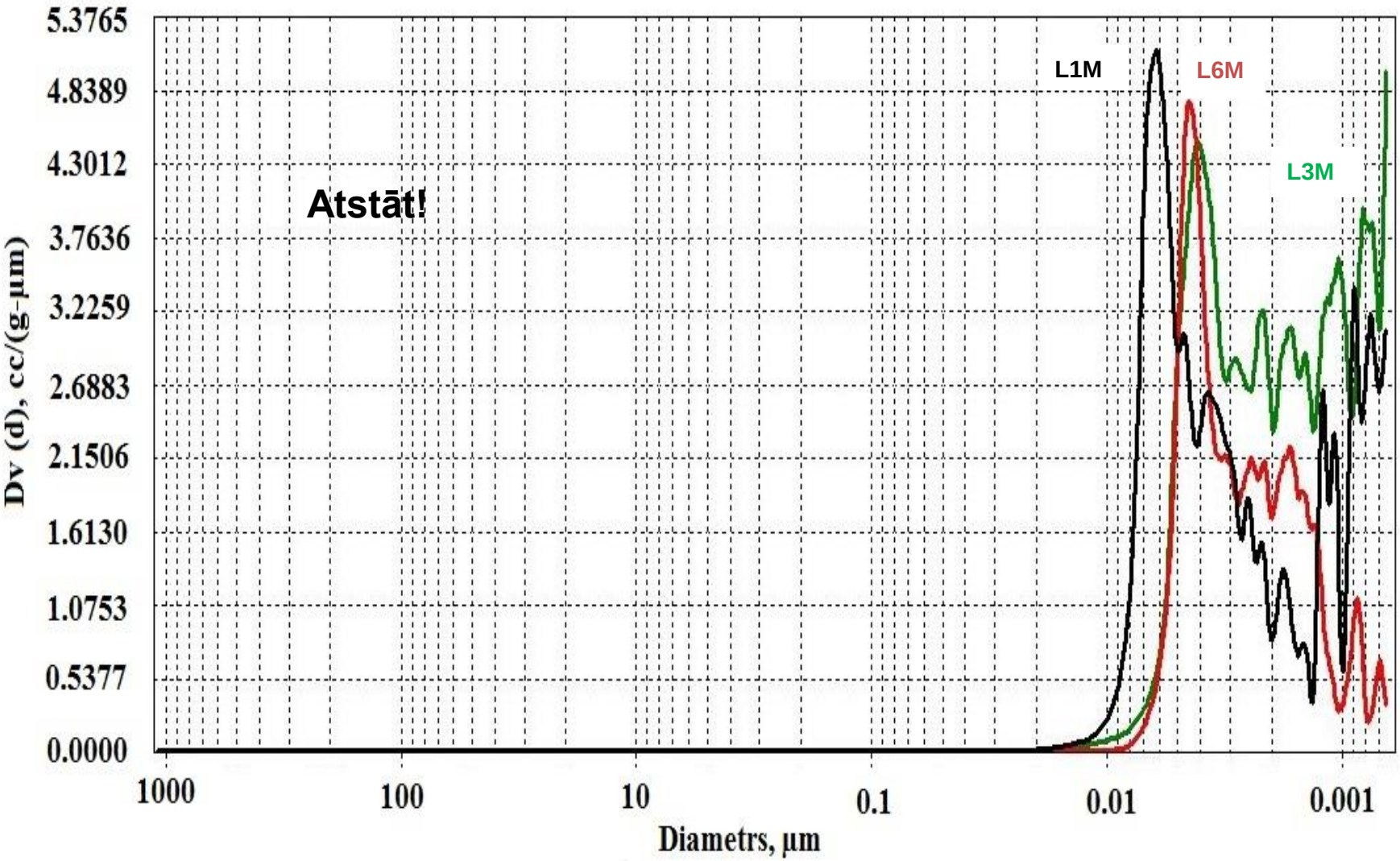


Fig. 11. Differential porosity development of sintered ceramic samples L on molar concentration of NaOH solution.

Results and discussion

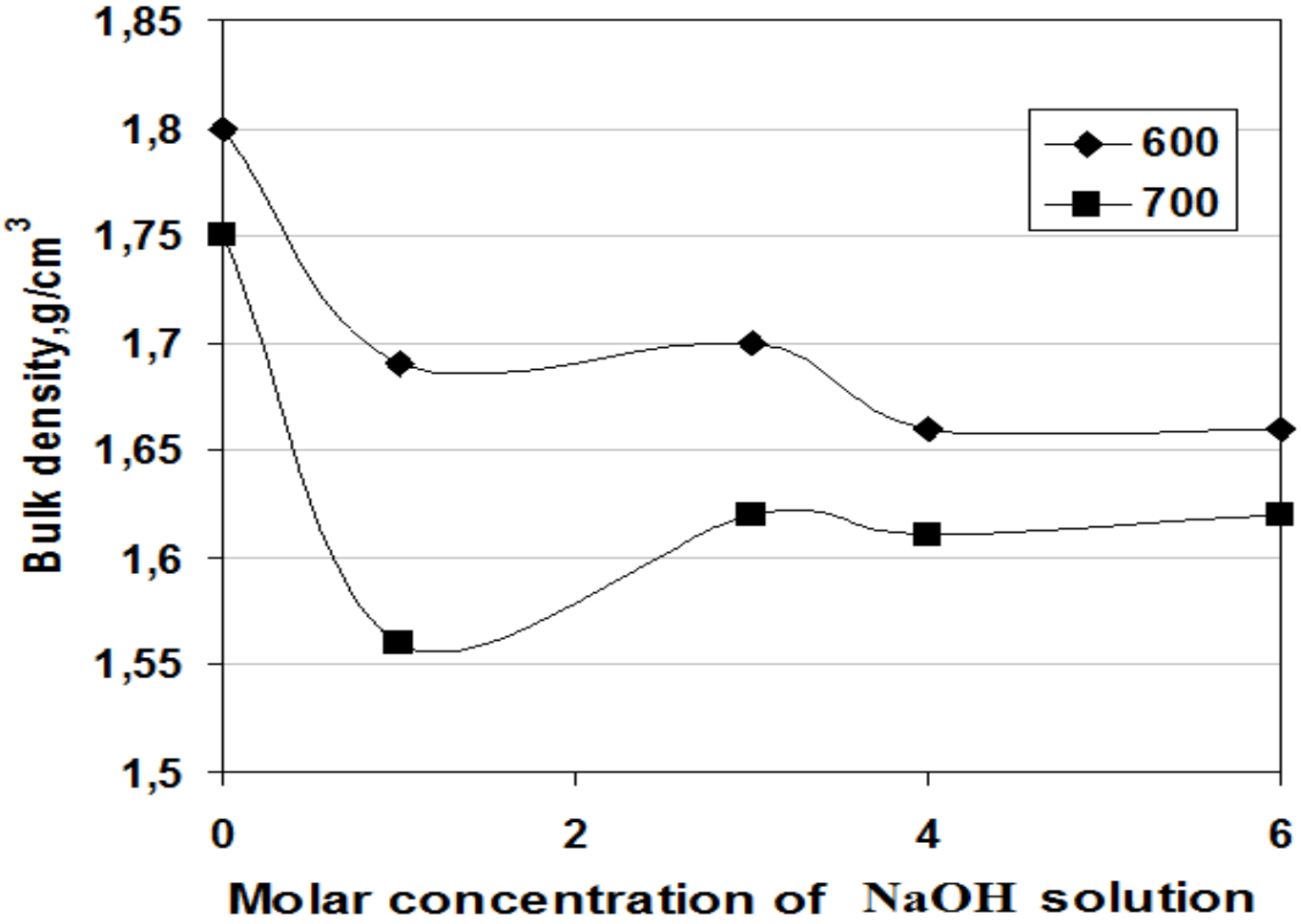


Fig. 8. Bulk density of ceramics samples in dependence of molar concentration of NaOH solutions.

Results and discussion

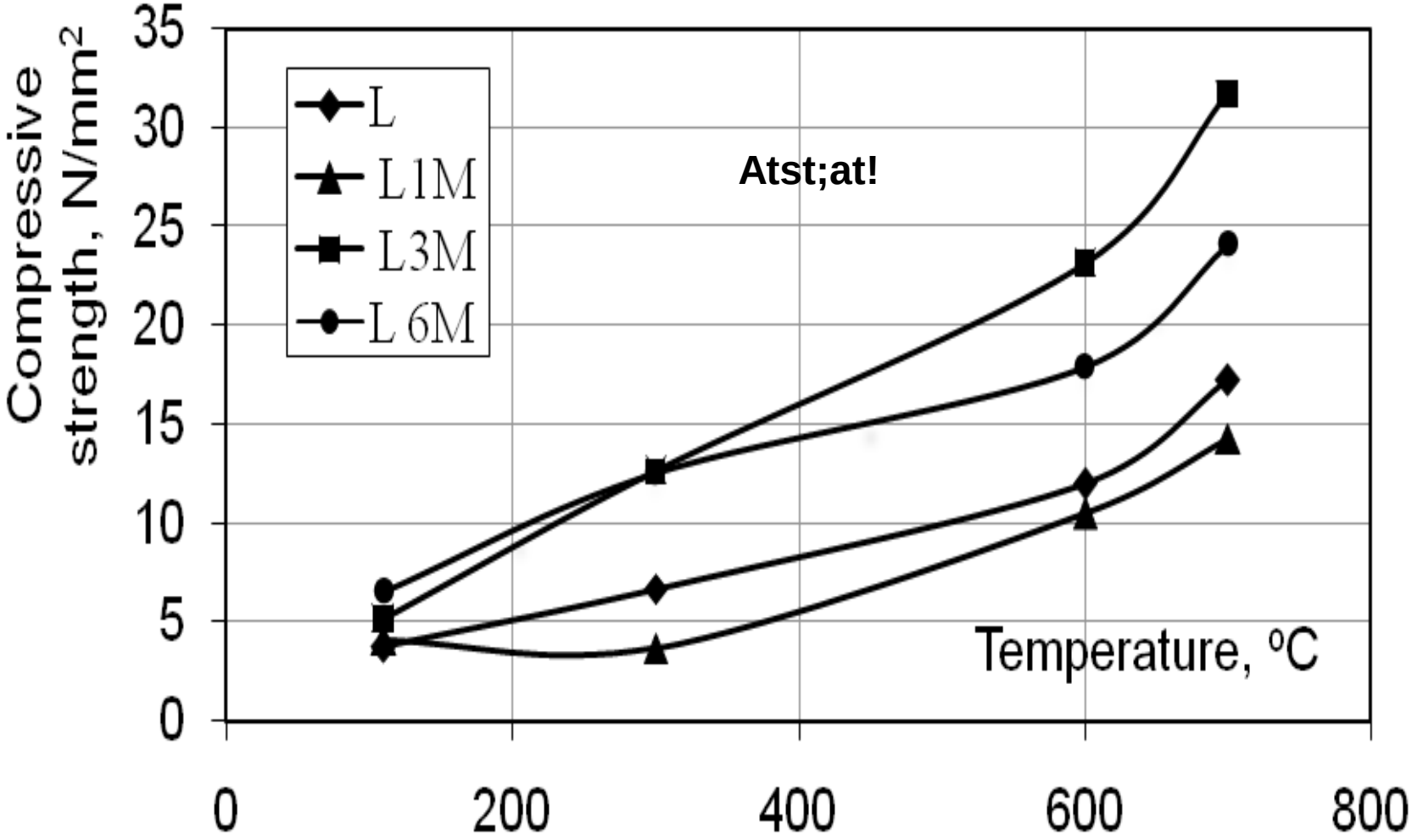


Fig. 9. Compressive strength of ceramics samples in dependence of molar concentration of NaOH solutions.

Results and discussion

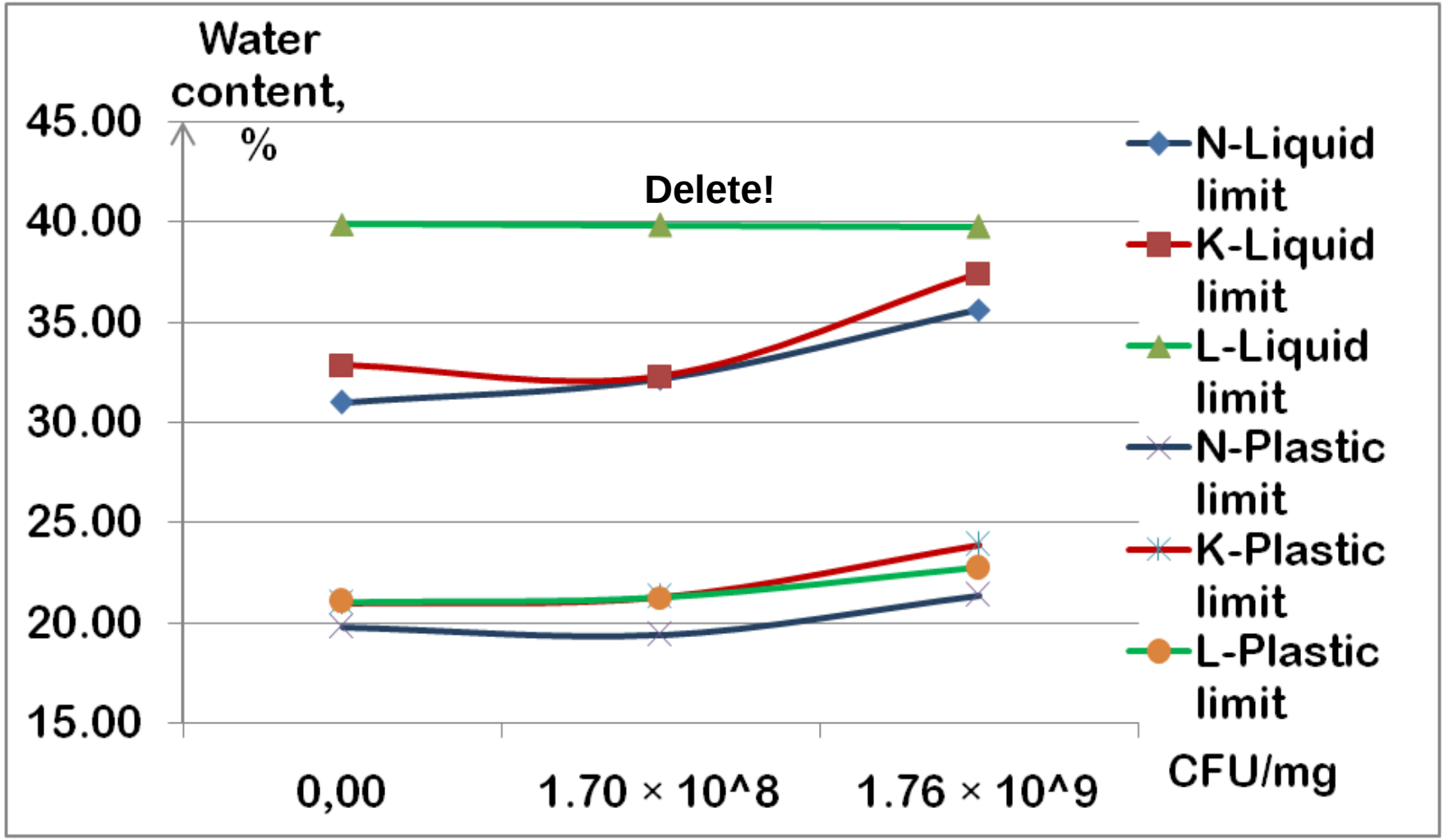
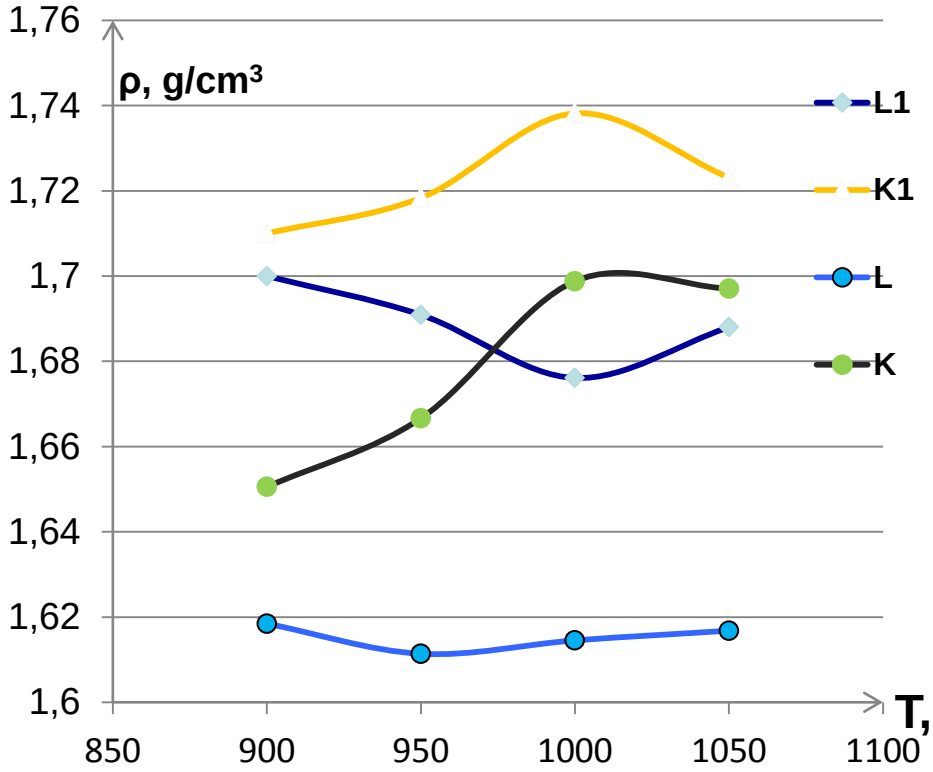
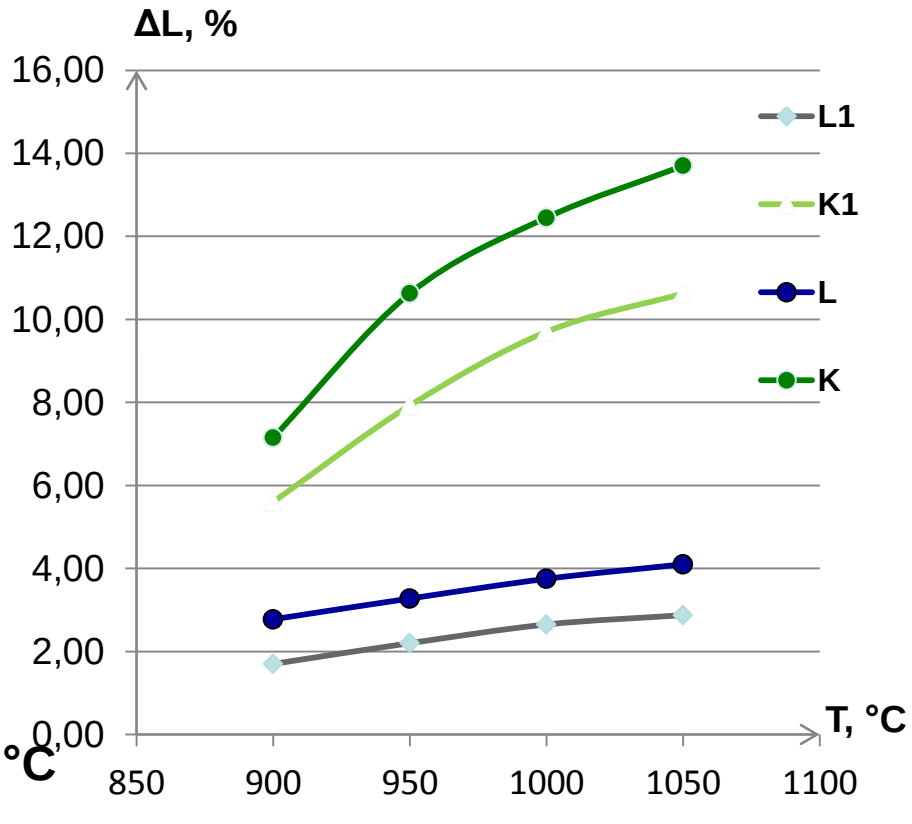


Fig. 10. Comparative characterization of flowability-degradation of three illite clay samples in dependence on bacteria *Ps. Fluorescens AM PS11* concentrations.

Results and discussion



a)



b)

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Fig. 11. a) and b). Bulk density and shrinkage change on sintering temperature.

Conclusion

- Alkaline with a sodium hydroxide of not dehydroxylated layered alumosilicate – illite clay has been studied.

- This study shows that alkaline activation of raw illite clay by sodium hydroxide 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 all crystalline phases for illite and kaolinite and with illite structural water losses characterized by DTA.

- It is shown on considerable influence of chemically treatment on some properties of sintered samples in temperature range from 100 °C to 700 °C ceramic samples. In particular there are noticeable changes of total porosity and bulk density as well as increase of compressive strength in the whole sintering temperature interval by reaching maximum values of > 30MPa at 700°C.

Thank You