Use of Differential Treatment of Illite to Modify Their Structure and Properties

Gaida Sedmale[1], Martins Randers[2], Liga Grase[3], Juris Kostjukovs[4],
[1–3]Riga Technical University, [4]University of Latvia

Abstract — **Influence of chemical, mechanical and thermal treatment on structure and properties of illite and impact on development of high-temperature ceramics was investigated. The object of this study was illite from Quartenary glacio-limnic clay of state importance deposit Apriki. Treated clay fractions were subjected to X-ray diffraction, SEM and differential thermal analysis.**

It was found that thermal and chemical treatment is effective. Thermally treated illite with $Al(OH)_3$ additive was used for sintering a new dense ceramic compositions. Ceramics were characterized by bulk density, shrinkage and compressive strength $150-165$ N/mm^2.

Keywords — **Ceramics, illite, properties structure, treatment.**

I. INTRODUCTION

Illite is one of the most common clay mineral in earth surface. Its definitions and characterization criteria have fluctuated [1]. Commonly illite is described as a clay mica with a general composition of $K_xAl_x(Si_{4-x}Al_x)O_{10}(OH)_2$ (where $0.75 < x < 0.9$). Structurally illite belongs to sheet silicates where structural units consist of two Si-O tetrahedral sheets always joined with an octahedral Al-O sheet. Conceptually this is accomplished by having the apical oxygen anions of the tetrahedral sheet to form a part of an immediately adjacent octahedral sheet. To accomplish this, an OH$^-$ from the octahedral sheet must be removed to make room for each apical oxygen anion from tetrahedral sheet [2]. Both sheets are combined to form layers known as 1:1 and 2:1 layers. Due to the substitution of cations in tetrahedral and octahedral sites of clay mineral for 2:1 type varieties of structures are characteristic. Often as a result of isomorphous substitution variable amounts of iron, magnesium, alkali metal, alkali earth and other cations are present in the interlayer space or in lattice framework.

Clay minerals have a wide range of particle sizes from tens of angstroms to millimeters. Many clay minerals form sheet-like particles or platelets. In particular, the thickness of each clay mineral layer is around one nanometer, e.g., 0.96 nm for montmorillonite [3]. These characteristics of clay minerals show that they could have a significant potential in manufacturing and environmental industries through new processes and approaches.

One of more investigated processes to attain an increased compressive strength of materials containing clay minerals is by development of proper mix with, e.g., [4], [5], highly alkaline solution. Although 1:1 layer lattice alumosilicates, i.e., geopolymers, are mainly used for this preparation, it is also of interest to use 2:1 minerals such as 2:1 illite. It was shown [6], [7] that for illite analogue — pyrophillite with unit

structure $Al_2AlSi_3O_{10}(OH)_2$, in which the octahedral Al-O sheet is enclosed above and below by two tetrahedral Si-O — attempts to produce fully reacted alumosilicates (geopolymers) was unsuccessful. Dehydroxylation of pyrophillite at 800 °C produces significant changes in Al coordination, but does not form a viable geopolymer.

It was suggested that inability to form viable geopolymers may be due to the retention of the crystalline 2:1 layer structure in pyrophillite and its dehydroxylated phase. According to the authors [6], the enclosed AlO_6 sheet by the upper and lower SiO_4 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 formation geopolymeric materials that attain reasonable hardness and strength at 60 °C. These materials are not fully X-ray amorphous, but X-ray powders show traces of zeolitic phases.

In [8] it is concluded that burning conditions of illite-smectite clays remarkably influence the molar ratio of Si/Al. There it is shown that burning in reducing atmosphere enhances the thermal reactions of illite-smectite and illite clays. The activation in alkaline solution of thus treated clays indicates intensive dissolution and polycondensation of the alumosilicates.

The aim of this study is to show how chemical, mechanical and thermal treatment conditions influenced the structure and some properties of treated illite, as well as impact of its development on dense high–temperature ceramics.

II. EXPERIMENTAL PROCEDURE

In this study Quartenary glacio-limnic clays from a clay deposit of national importance, Apriki, were used [9]. Clay samples were taken from $1.5-2$ m depth.

Apriki clay forms a clay deposit of national importance and in general has a fair amount of carbonates and high illite/kaolinite clay fraction content (particles < 0.005 μm, up to 86 %). The mean SiO_2/Al_2O_3 weight ratio for clay is in the range of $3.20-3.45$.

Clay fraction (illite) from Apriki clay was separated using sedimentation and chemical methods [10].

Supplementary materials for chemical treatment of illite were NaOH pellets for preparation of 3 M, and 6 M NaOH water solutions. Mechanical treatment was performed by intensive milling in a planetary mill *Retsch PM-100* for 10 h, thermal treatment — by processing at 600 °C for 30 min in *Nabertherm-3000* furnace.

For characteristization of treated and non-treated illite as well as sintered ceramic samples X-ray diffraction analysis was used (XRD model *Rigaku*, Japan, and *D8 Advance Bruker*

AXS with CuK$_a$ radiation at scanning interval 2θ 10−60° and speed 4°/min), SEM *Nova-Nano 650* (*FEI Netherlands*) also was used. To perform elementary (oxide) analysis for illite, X-ray spectrometer *S4 PIONEER* (*Bruker AXS*) was used.

Differential thermal analysis (*Setaram, SETSYS Evolution-1750*) was applied to characterize the phase changes after thermal treatment of illite.

Four differently treated illite samples were used: **ap 0** — not treated, **ap 1** — milled in a planetary mill *RETSCH PM-100* for 10 h, **ap 2** — treated with 3 M NaOH, **ap 3**- treated with 6 M NaOH, each for 24 h at 50 °C and **ap 4** — thermally treated at 580 °C for 30 min .

Samples for ceramic development were prepared as cylinders with height 30 mm and diameter 25 mm and subjected to different firing schedules in air at maximum temperatures 800 °C, 900 °C, 1000 °C and 1100 °C (heating rate was 5−6 °C/min, holding time at maximum temperature was 30 min).

Some ceramic properties were established in accordance with EN. The compressive strength was determined using *Toni-Technic* (*Baustoffprüfung*) model *2020*.

III. RESULTS AND DISCUSSION

Clay fraction phases and elementary (oxide) composition of both sedimentary and chemically separated fraction is presented in Fig. 1. As can be seen from both phase and oxide compositions they are somewhat shifted. The content of main components (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO and TiO_2) of clay fraction for Apriki clay correlate for both methods and is shifted not more as 2.9% for Al_2O_3 and for SiO_2 2.2 %. Molar ratio of SiO_2/ Al_2O_3 was not higher than 1.05−1.10 (mass ratio 1.65−1.75); this is relatively low for geopolymer reactions.
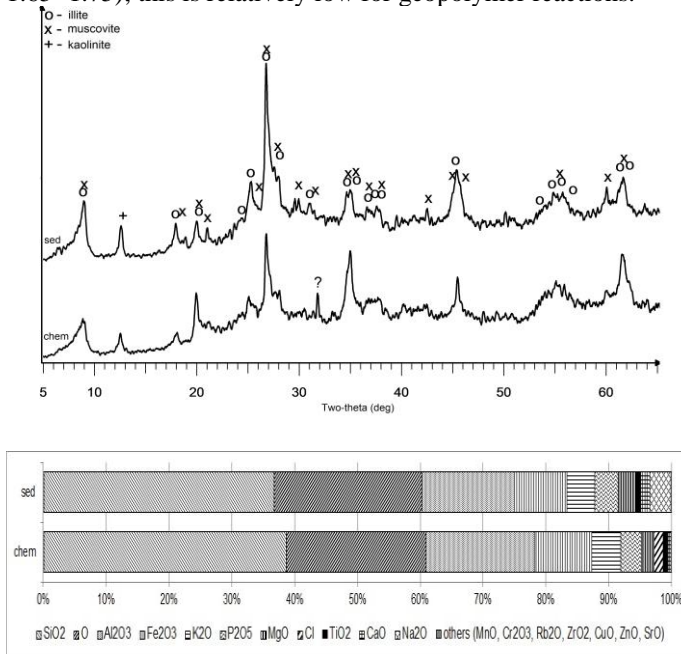

Fig. 1. Phase and oxide composition of clay fraction, sedimentary and chemically separated.

Our previous studies [11] showed that the pre-thermal treatment of illite clay at temperature up to 600 °C influenced

its reaction potential, but formation of typical geopolymer binders could not be observed here.

The XRD patterns showed that impact of chemical, mechanical and thermal treatments on the change of intensity of diffraction peaks of illite (which could characterize that the breakdown of illite structure) was insignificant.

It should be noted that treatment of illite by 6 M NaOH solution led to formation of a new phase — sodium aluminium silicate hydrate. Despite of the fact that illite structure in this case was not destroyed, compounds with weak binding properties appeared.
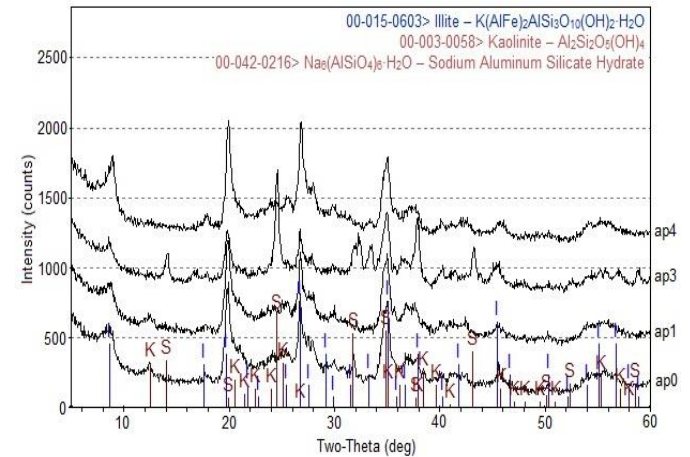

Fig. 2. XRD patterns of differential treated illite: ap-0 — not treated, ap-1−milled for 24 h, ap-3 — treated with 6 M NaOH, ap-4 — pre-thermal treatment at 580 °C for 1 h.
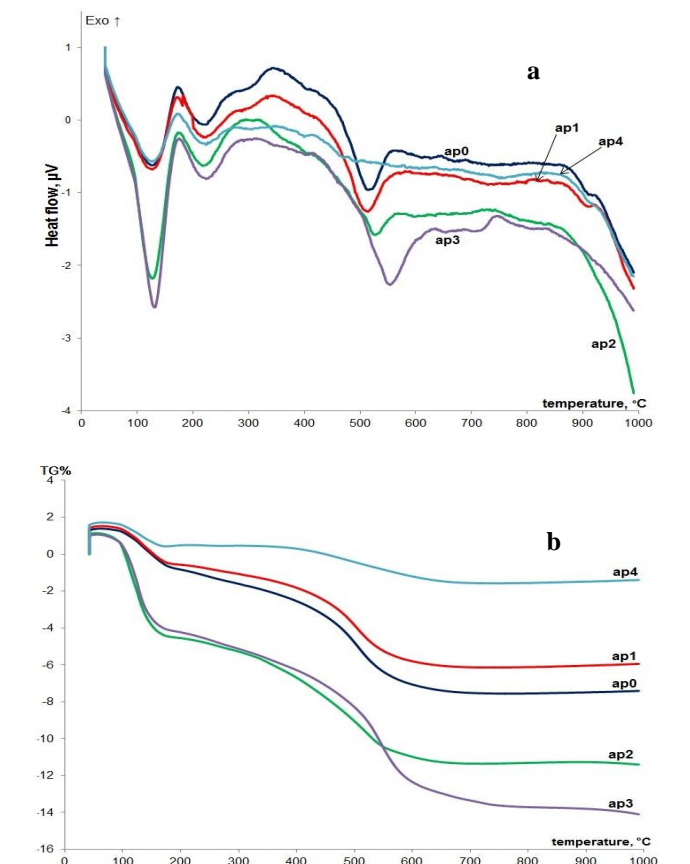

Fig. 3. DTA (a) and TG-curves (b) of differently treated illite: ap-0 — not treated, ap-1 — milled for 24 h, ap-2, 3 — treated with 3 M and 6 M NaOH, ap-4 — pre-thermal treatmentat 580 °C for 1 h.

In its turn DTA indicated significant changes in illite for the thermally treated sample ap-4 in temperature range up to 550 °C (Fig. 3). As it is known [11], this is associated with the release of structural water from illite. For other treated samples the DTA curves seemed similar with a little shifted exo-effect at the lowest temperatures. For the samples treated with 6 M (and 3 M) NaOH there was an increase in the loss of weight (TG-curves).

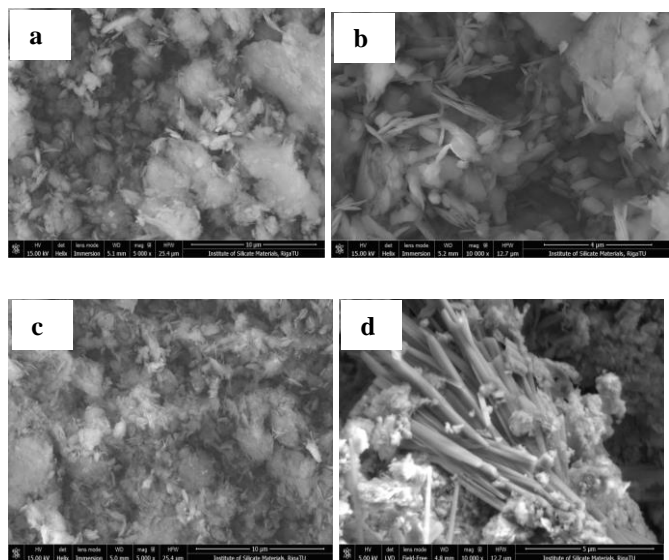Scanning electron micrographs of clay fraction powder before and after treatment are shown in Fig. 4.

Fig. 4. SEM micrographs of illite powder: a — illite chemically separated from clay, b — illite separated from clay by sedimentation, c — thermally (at ~580 °C) treated illite, d — illite treated with 6 M NaOH.

Both chemically and sedimentary separated illite seemed somewhat different. In both cases irregular particles and platelets formed (Fig. 4 a, b), especially for illite separated from clay by sedimentation (Fig. 4 b). Particle or agglomerate size distribution wass broad. Thermal treatment yielded homogenous illite powder mixture (Fig. 4 c) with particles that had almost spherical shape, which would promote sintering [12]. Significantly differs illite sample treated by 6 M NaOH. It is possible to observe formation of new needle-shaped crystalline phase — sodium aluminosilicate hydrate $Na(AlSiO_4)_6 \cdot H_2O$ which pervades illite.

Next experiments were carried out using compositions of pretreated illite (as more active from processed illite) with 20−50 wt% of $Al(OH)_3$ additive to obtain dense hightemperature ceramics at lowered temperature. Visually the sintered samples from compositions of pre-treated illite-$Al(OH)_3$compositions at temperatures ranged from 800 °C to 1100 °C look as follows in Fig. 5.

As is visually shown, all samples had obvious and remarkable shrinkage as well as change of color that was more pronounced in samples with higher illite content in starting compositions. Samples sintered at 1000 °C were characterised by high compressive strength. These values (as well as values for shrinkage) changed depending on temperature and are displayed in Fig. 6.
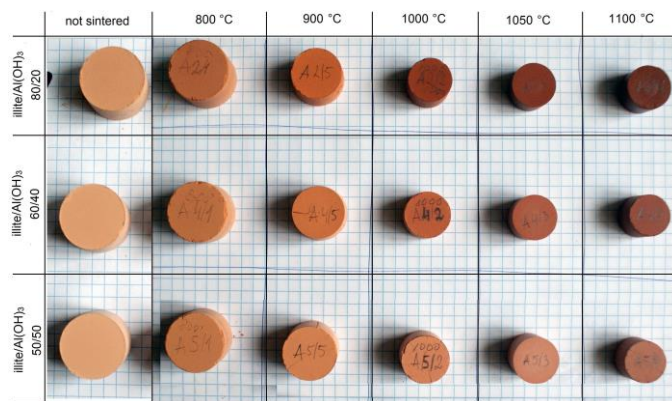

Fig. 5. Samples from compositions 80–50 % at 600 °C pre-treated illite — 20–50 % Al(OH)3 sintered at different temperatures.

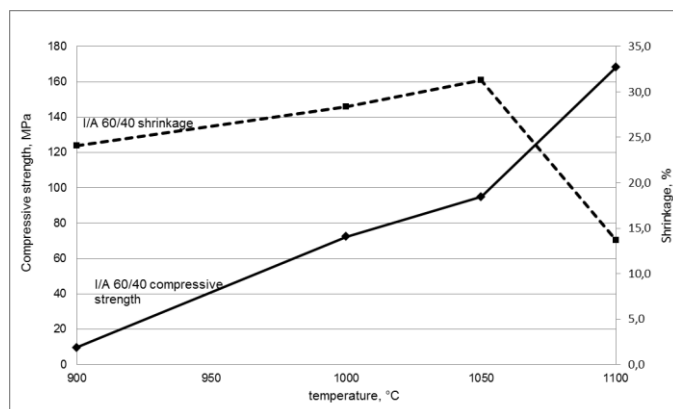**Fig. 6.** Dependence of compressive strength and shrinkage on temperature for sample 60 % pre-treated illite — 40 % $Al(OH)_3$.

IV. CONCLUSION

Thermal, chemical and mechanical treatment of illite separated from clay deposit Apriki (a deposit with national importance), were used to modify illite structure.

Thermal treatment at temperature ~600 °C and chemical treatment with 6 M NaOH were more effective treatments. Thermal treatment yielded homogenous illite powder with particles that had almost spherical shape that would promote sintering. Chemical treatment with 6 M NaOH led to formation of a new crystalline phase — sodium aluminosilicate hydrate $Na(AlSiO_4)_6 \cdot H_2O$ — that pervaded illite.

Thermally treated illite was used for development of new compositions with $Al(OH)_3$. After sintering samples at 1000–1100 °C with 40 % $Al(OH)_3$ additive it was found that compressive strength of ceramics reached value 168 N/mm^2.

REFERENCES

1. **Meunier A., Velde B**. *Illite: Origin, Evolution and Metamorphism*. Springer, New York, 2004. http://dx.doi.org/10.1007/978-3-662-07850-1
2. **Nesse, W.D.** *Introduction to Mineralogy*. Oxford University Press, New York- Oxford, 2000. pp. 235–260.
3. **Chuan, Hui Zhou, Keeling, J.** Fundamental and applied research on clay minerals: from climate and environment to nanotechnology. *Applied Clay Science*, 2013, vol. 74, pp. 3–9. http://dx.doi.org/10.1016/j.clay.2013.02.013
4. **Duxson, P., Grant C., Lukey, G.C.,** et al. The thermal evolution of metakaolin geopolymers: Part 2-Phase stability and structural

development. *J. Non-Cryst. Solids*, 2007, vol. 353, pp. 2186–2200. http://dx.doi.org/10.1016/j.jnoncrysol.2007.02.050

5. **Mac Kenzie, K.J.D., Brew, D.R.M., Fletcher, R.A.** et al. Formation of alumosilicate geopolymers from 1:1 layer-lattice minerals pre-treated by various methods: a comparative study. *J. Mater. Sci.*, 2007, vol. 42, pp. 4667–4674. http://dx.doi.org/10.1007/s10853-006-0173-x

6. **Buhwald, A., Hohmann, M., Posern, M.,** et al**.** The suitability of thermally activated illite/smectite clay as raw material for geopolymer binders. *Applied Clay Science*, 2009, vol. 46, pp. 300–304. http://dx.doi.org/10.1016/j.clay.2009.08.026

7. **Mac Kenzie, K.J.D., Meinhold, R., Brown, H**.et al. Thermal reactions of pyrophillite studied by high-resolutions solid-state ^{27}Al and ^{29}Si nuclear magnetic resonance spectroscopy. *J. Am. Ceram. Soc.*, 1985, vol. 68, pp. 266–272. http://dx.doi.org/10.1111/j.1151-2916.1985.tb15320.x

8. **Seiffahrth, T., Hohman, M., Posern, K.,** et al. Effect of thermal pre-treatment conditions of common clays on the performance of clay-based geopolymers binders. Applied Clay Science, 2013, vol. 73, pp. 35–41. http://dx.doi.org/10.1016/j.clay.2012.09.010

9. **Stinkule, A., Stinkulis, G**. *Latvian mineral raw materials*, Latvian University Publishing House, 2013 (In Latvian).

10. Latvijas universitāte. *Method for separation of submicron particles of illite mineral from illite clay*. Kostjukovs, J., Truba-Boginska, A., Actins, A. int. Cl.: C01B 33/40, EP 2840063A1, 25.02.2015 Bulletin 2015/09.

11. **Segliņš, V., Sedmale, G., Šperberga, I.** Ģeopolimēru tehnoloģijas pielietojums zemtemperatūras keramikas produktu izstrādei. *Material Science and Applied Chemistry*, 2012, vol. 26, pp. 9–21 (in Latvian).

12. **Sahnoune, F., Chegaar, M., Saheb, P.,** et al. Algerian kaolinite used for mullite formation. *Applied Clay Science*, 2008, vol. 38, pp. 304–310. http://dx.doi.org/10.1016/j.clay.2007.04.013

Gaida Sedmale, *Dr. habil. chem.* (1989), asoc. prof./leading researcher, is the author of more than 200 scientific publications in the field of glass and ceramic chemistry and technology. The main outputs of research on glassy and ceramic materials are protected by more than 50 Latvian and Russian patents. For the last 20 years her scientific interest has been connected with new high-temperature and traditional ceramic materials; she also is involved in research on Latvian illite clay and output of materials.
Address: 3/7 Paula Valdena Str., LV-1048, Riga, Latvia
Phone: +371 67089257, Fax: +37167615765
E-mail: gsedmale@ktf.rtu.lv

Martins Randers, *B. sc. geol.* (2010), is a 3rd year bachelor level student of Materials Science programme at Riga Technical University (RTU), Faculty of Materials Science and Applied Chemistry. He also is a laboratory assistant at the Institute of Silicate Materials, RTU. His field of study is clay chemistry and ceramics.
Address: 3/7 Paula Valdena Str., LV-1048, Riga, Latvia
E-mail: martins.randers.@inbox.lv
     martins.randers@rtu.lv
Phone: +371 27876821

Liga Grase, *Mg. sc. ing.* (2012), is a doctoral student and a researcher at Riga Technical University, Faculty of Material Science and Applied Chemistry, Institute of Silicate Materials,. She is interested in chemical technology, materials science, nanotechnology, particularly in structure of materials and morphology measurements of inorganic materials using high resolution scanning electron microscope.
Address: 3/7 Paula Valdena Str., LV-1048, Riga, Latvia
E-mail: grase.liga@gmail.com
     liga.grase@rtu.lv
Phone: +371 67089217

Juris Kostjukovs is a doctoral student and a researcher at the Department of Physical Chemistry, Faculty of Chemistry, University of Latvia. His major scientific interest is clay and clay minerals, smectites. He is the author of several patents and publications about smectite clay.
Address: Kr. Valdemāra 48, LV-1013, Riga, Latvia
E-mail: jukos54@gmail.com

Gaida Sedmale, Mārtiņš Randers, Līga Grase, Juris Kostjukovs. Diferencētas apstrādes pielietojums illītu struktūras un īpašību modificēšanai.

Pētīta ķīmiskas, mehāniskas un termiskas apstrādes ietekme uz illītu struktūras un īpašību izmaiņām, kā arī šīs apstrādes nozīme blīvu augsttemperatūras keramiko materiālu izstrādē. Par izpētes objektu bija izvēlēti kvartāra māli no Apriķu atradnes, kas ir valsts nozīmes māla atradne. Māli no šīs atradnes ir pieskaitāmi pie karbonātus mazsaturošiem māliem un tiem ir relatīvi augsts mālainās frakcijas saturs (daļiņas ar izmēru < 0,005 µm). Mālu frakciju (illīti/kaolinīts) izdalīja no māliem, pielietojot sedimentācijas un ķīmisko metodi. Pētījumiem pielietota ķīmiski izdalītā mālu frakcija. Šīs frakcijas ķīmiskai apstrādei ir pielietots 3 M un 6 M NaOH ūdens šķīdums, mehāniskai apstrāde bija 24 hilga intensīva malšana planetārajās dzirnaviņās, termiskā — izkarsēšana 600 °C temperatūrā 30 min. Neapstrādāto un apstrādāto illītu raksturojumam pielietoja rentgena fāžu analīzi (XRD modelis *Rigaku*, Japāna un *D8 Advance Bruker AXS*). Elelementu/oksīdu analīzi veica ar XRD spektrometru (*S4 PIONEER Bruker AXS*). Daļiņu morfoloģijas un sastāva izmaiņu izpētei pielietoja skenējošo elektronmikroskopu *Nova-Nano 650* (*FEI Netherlands*). Diferenciāli termiskā fāžu pāreju analīzi veica ar iekārtu *Setaram*, *SETSYS Evolution-1750*. Ir parādīts, ka sedimentāri un ķīmiski izdalīto illītu/kaolinīta fāžu sastāvs, kā arī oksīdu analīze ir nedaudz nobīdīti. Bija vērojamas arī daļiņu morfoloģijas atšķirības — sedimentēto illītu plākšņveida morfoloģija bija izteiktāka nekā ķīmiski iegūto. Rentgena fāžu analīze rāda, ka saistībā ar intensīvi malto un ar 3 M NaOH šķīdumu apstrādāto illītu/ kaolinīta fāžu difrakcijas maksimumu izmaiņas ir niecīgas. Maz izmaiņu novēroja arī DTA rezultātos. Savukārt, termiski apstrādātie illīti ir daļēji destrukturēti, pie ~ 600 °C izdalījās struktūras OH- grupas. Izmaiņas pēc apstrādes ar 6 M NaOH šķīdumu arī ir attiecināmas uz illītu struktūras izmaiņām, veidojoties nātrija alumosilikāta hidrātam Na(AlSiO$_4$)$_6$·H$_2$O, kurš, cauraužot illītus, tos "sacementē". Termiski apstrādātie illīti ir aprobēti kā saķepšanu veicinošs komponents jaunu keramikas kompozīciju izveidošanai ar Al(OH)$_3$. Ir parādīts, ka 60 masas % termiski apstrādātu illītu piedeva pie Al(OH)$_3$ apdedzināšanas temperatūrā > 1050 °C veido blīvu keramikas materiālu ar augstu spiedes izturības vērtību — 168 N/mm^2.