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Characteristics of Illite Clay and its Use for High - and Low Temperature Ceramics

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Abstract. Two ways for practical use of illite clays were studied: chemical treatment and non-conventional application to promote sintering and formation of mullite –ZrO_2 ceramics

It is shown that treatment of the illite Quaternary clay by KOH leads to forming of the weakly connected illite structure. That results in significant decrease of sintering temperature of the obtained ceramic materials. Use of Devonian clay as additive 8 wt.% for mullite – ZrO_2 ceramics leads to growth of its density and considerable increase of the compressive strength by maintenance of ZrO_2 in tetragonal crystalline form.

Keywords: illite clay, ceramics, geopolymer technology

1. INTRODUCTION

Deposits of clay - one of the most important mineral raw materials of the Phanerozoic sedimentary cover the territory of modern Latvia. Devonian clay accumulated together with sand and silt material in the shallow epeiric sea environment. The sand and clay deposition was intermittent due to changing clastic supply and likely altering water depth. Clay particles, as well as coarser silt and sand material were transported into the basin from northerly source areas – the Scandinavian Caledonides and the Fennoscandian Shield [1]. The finest clay particles settled down in local slump depressions at the delta front environment [2]. The Devonian clay is composed of illite with the admixture of up to 12-15 % of kaolinite and some chlorite. It is important to note that Devonian deposits regardless of their considerable geological age contain plastic, almost unconsolidated clay material.

Quaternary clay deposits were mostly formed in the glacial meltwater basins. Seasonal changes of ice melting intensity often caused pulsating influx of sand and silt particles, therefore many clay deposits have rhythmically layered (varved) structure. The Quaternary clay minerals also are dominated by illite (75-80%) with admixture of chlorite. A few practically useful clay deposits have been formed also after glacier retreat – during ancient stages of development of the Baltic Sea. The main difference in the Devonian and Quaternary clay deposits is the content of carbonates. The Devonian clay generally has a small amount of scattered carbonate admixture, but in several deposits the quality of clay is reduced due to hard dolomite inclusions. Quaternary clay typically is rich in fine, scattered carbonates, but hard, harmful inclusions of these minerals are rare [3].

The Devonian and Quaternary clays are used for production of conventional ceramic products such as building bricks, blocks, roof tiles, pottery, as well as sorbents. Moreover, they were added in the percentage of 35 wt. % to a mixture composed of feldspar and quartz sand to produce stoneware tiles. It is shown [4] that the presence of illite inhibits the formation of mullite and cristobalite, since silica and alumina tend to form alkaline glass. The presence of small amount of goethite in this clay promotes the formation of mullite, which could eventually host Fe in its structure. In [5] it is also indicated that use of kaolinites with different content of structural iron and crystallinity degree reveals its impact on incorporation into mullite in octahedral sites, and crystallisation kinetic of mullite.

In our previous studies [6] we emphasized the influence produced by a small amount (8.0-8.5 wt. %) of illite additive on mullite -ZrO_2 (tetr.) phase formation in mullite –ZrO_2 ceramics.

This study presents two ways for use of illite clays: geopolymers – the purpose of which is to show the effect of alkalines on transformation of Quaternary clay/illite structure and in its turn – on some ceramic properties (bulk density, porosity) and compressive strength, while non - conventional application is to promote sintering and consecutive high-temperature crystalline phases formation in dense ceramics.

II EXPERIMENTAL PROCEDURE

Two types of clays - Quaternary **Q** and Devonian **D** from Latvia and the two compositions with (and without) additives of these clays – were used for development of dense mullite-ZrO_2 ceramics. The chemical composition of both clays is given in Table1 [3].

TABLE 1.

CHEMICAL COMPOSITIONS OF CLAY Q* AND D** (WT.%)

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
Clay Q	54.56	14.69	5.47	0.59	8.27	2.52	3.35	0.53
Clay D	50.5	20.8	7.5	0.8	1.9	3.6	5.0	0.1

*- Ignition loss at 1000 °C – 10.02; ** - Ignition loss at 1000 °C - 9.8

Quaternary clay samples were taken in the Ane pit. All samples represent intermediate composition of clayey material used to produce bricks and ceramic building blocks. They were taken from the wall of actively exploited pit by linear sampling method to represent intermediate composition of commercial beds.

Devonian clay samples were obtained in the Liepa (Lode) pit. Samples were taken from technological sheet-like pile created in a step-by-step mining and redepositing of mined material. Such an artificially layered technological pile, which is kept in open-air conditions for several seasons, including frost-thaw processes, allows to regain homogeneity and plasticity of the clay material and to preserve permanent quality of the raw material for its practical use. Linear sampling method was also used to represent intermediate composition of technological sheet-like pile.

The composition of D-clay used for high-temperature ceramics development is shown in Table 2.

TABLE 2

COMPOSITIONS FOR HIGH-TEMPERATURE MULLITE-ZrO_2 CERAMICS

Sample	γ Al_2O_3	SiO_2.n H_2O SiO_2- 85%	ZrO_2	Y_2O_3	Illite clay D
10	62.30	28.00	5.20	4.50	-
10i	57.30	25.85	4.70	4.15	8.00

For obtaining the initial powders of clay Q, the raw dried clays were ball-milled in the laboratory mill for several minutes, and so were compositions -10 and 10i, but for a different length of time.

Technological ways of formation/study of geopolymers (I) and ceramic products (II**)** include the following steps and objects:

(I) Q-clay powder - treatment by 1M, 3M and 6M KOH solution for 24h at 50^0C

→IR-spectroscopy → shaping of samples→ drying and sintering at temperatures 700-900^0C→ XRD, bulk density, open porosity;

(II) initial mixtures prepared by planetary milling for a different length of time (4 - 24 hours) →forming of dry powders by axial pressing →sintering at temperatures from 1100 to 1300^0 C (1h) → XRD, SEM, density, compressive/bending strength.

The equipment used: the planetary laboratory mill Retsch PM 400; for IR-spectroscopy – spectrophotometer IR prestige-21(FTIR-8400S); XRD-model Rigaku, Japan, with CuK_α radiation at scanning interval from $2\theta = 10...60^0$; the microstructure of sintered ceramic samples wasdetermined by scanning EM, model JSM-T200, compressive/bending strength was determined by Toni-technic model 2020 and Zwick/Rolle model 1486.

Bulk density and open porosity of ceramic samples were determined in accordance with EN.

III. RESULTS AND DISCUSSION

The qualitative crystalline phase characteristics of both clays - Q and D are similar. Crystalline phases of quartz, dolomite and calcite predominate. Presence of crystalline clay minerals – illite, chlorite and kaolinite is not so pronounced. Usually the total amount of clay fraction (with the particle size less than 2 μm and determined by sedimentation analysis) in Quaternary **Q** clay is up to 50-55%, but in Devonian clay **D** the average share is 70-75 % [1]. The mineralogical composition of this fraction shows that illite is the dominating mineral there, Figure 1.

The effect of alkalines on transformation of Quaternary clay/illite structure shows the FTIR-spectra (Figure 2) of both the raw Q-clay and processed by 1M, 3M and 6M alkaline (KOH) – solution. Significant change in the two main oscillations as well as at 779 cm^{-1} for treated samples of clays are observed by:

– OH-stretching bands at frequency 3618-3626, 3441 and 3695 cm^{-1},

- spectral bands at 1435- 1427 cm^{-1}, and

- 779 cm^{-1}.

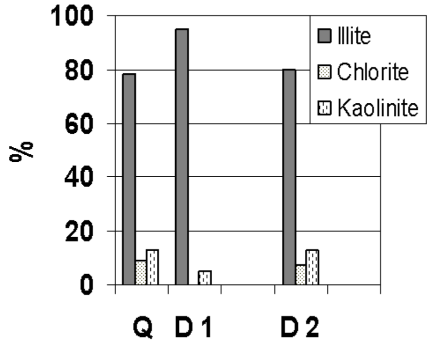

Fig. 1. Mineralogical composition of clay fraction for Q and D clays (D1-D carbonate beds, D2 –D siliciclastic beds).

The first three absorption bands appear and grow for treated Q-clay and can be related to O-Al-OH grouping, where O is associated with neighbour Si- layer. The bands at 1435-1427 cm^{-1} point at the appearance of new oscillations in treated Q-clay and obviously are related to development of K-O-Si bands [7, 8] band at 779 cm^{-1} – probably with 4 coordinated Al-O stretching vibration.

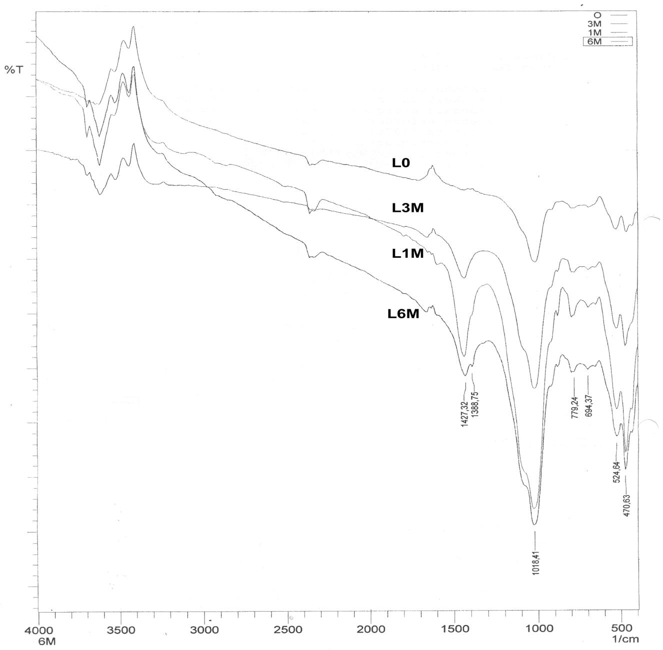

Fig. 2. FTIR spectra for raw Quaternary clay **(())** and the clay treated with 1M, 3M and 6M KOH .

The scheme of possible chemical processes of monomer development by treated Q-clay could be depicted by the following reactions:

$$\underset{\text{Illite}}{(K,H_3O)Al_2(OH)_2[AlSi_3O_{10}].nH_2O} + 3K^+ + 3\,OH^- \longrightarrow$$

$$\longrightarrow 3\,Al(OH)_3 + 3Si(OH)_4 + 4K^+ \xrightarrow{\text{or}}$$

$$\longrightarrow \underset{\text{Sodalite like zeolite}}{K_4Al_3Si_3O_{12} + n\,H_2O}$$

Sodalite (zeolite) should be the end product, which was not observed.

Comparison of XRD – patterns of both Q-clay and Q/KOH clay show that there are small changes in the illite as well as kaolinite crystalline phases peaks intensity for Q/KOH clay, Figure 3.

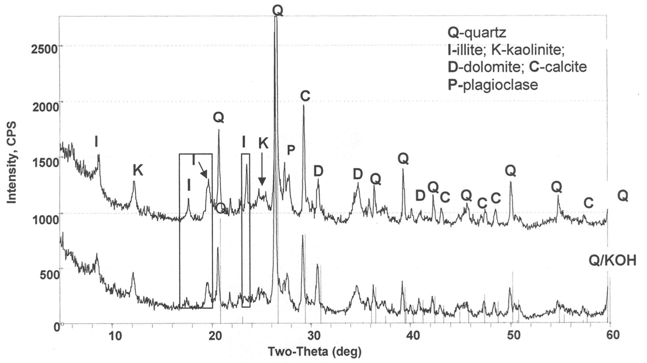

Fig.3. XRD patterns of Q-clay and treated by 3M KOH-solution.

The compressive strength of sintered samples at temperatures 750^{0}C to 900^{0}C show that for both sintered samples especially at higher temperature the compressive strength is significantly higher for the sample Q/KOH (Figure 4.) Overall, the bulk density has the tendency to go down. Its values in above mentioned temperature range change from 1.55 to 1.68 g/cm^3 for sintered samples from untreated clay and a little higher - 1.65 g/cm^3 to 1.72 g/cm^3 for the samples sintered from Q/KOH. Such inconsistency gives reason for further studies of the type of pores and their distribution in sintered samples.

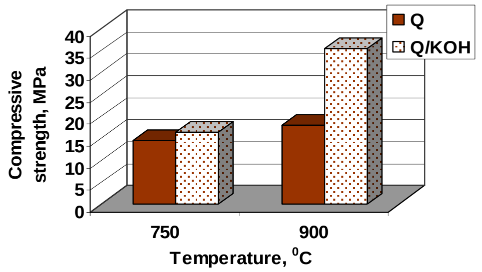

Fig.4. The compressive strength of sintered samples at temperatures 750^{0}C and 900^{0}C.

Another way to use illitic clays (non- conventional) was the application of D1 clay for production of dense mullite –ZrO_2 ceramics. That includes two considerations: to promote formation of high-temperature mullite and ZrO_2 (tetragonal phase) at lower temperatures along with the acceleration of densification process and to prevent the change of ZrO_2-tetragonal formed at higher temperature to monoclinic modification by cooling. Figure 5 shows the crystalline phase development for mullite – ZrO_2 ceramics at the sintering temperature 1250^{0}C, which is much lower than the temperature traditionally used for sintering mullite ceramics.

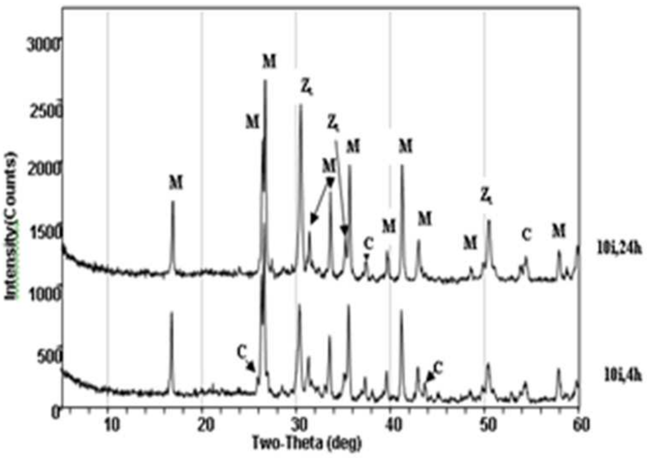

Fig.5. XRD patterns of ceramic from composition 10i milled for 4 and 24 hours and sintered at 1250^{0}C: M-mullite $3Al_2O_3.2SiO_2$, C-corundum α Al_2O_3, Z_t – ZrO_2 (tetr.).

Figure 6 shows the impact of illite clay D1 additive on the development of density and compressive strength of the mullite-ZrO_2 ceramics with and without illite clay additive.

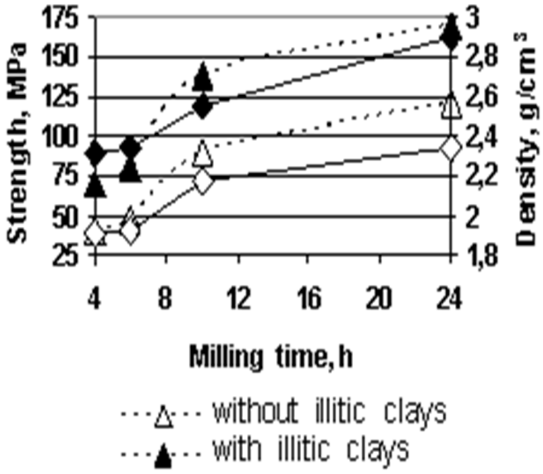

Fig.6. Strength (—) and density (----) - milling time relation of mullite-ZrO_2 ceramic samples with and without illitic clay additive.

It is obvious that both values are essentially accelerated by illite clay additive. Such determinative role could be connected to the structural relaxation at up to 700^{0}C together with liquid phase formation starting from this temperature and subsequent triggering of diffusion processes by sintering of mullite-ZrO_2 ceramics.

IV. CONCLUSIONS

Use of the Quaternary and Devonian clay of Latvia for development of various ceramic materials is considered.

Treatment of the illite Quaternary clay with KOH changes illite structure, but does not destroy it. Main changes could be related to the changes of O-Al-OH grouping where O is associated with the neighbouring Si- layer and with the penetration of K^+ between Si-O and Al-O layers.

The ceramic materials developed from chemically treated Quarternary clay and consolidated at 750^{0}C have the compressive strength comparable with the same values for the respective ceramic products sintered at 900 ^{0}C.

Significant increase of the density and compressive strength is observed when just 8 wt.% Devonian illite clay is used as an additive for development of mullite $–ZrO_2$ ceramics.

Respective values of these properties, when compared to ceramics without clay additive, show that density of the samples with this additive increases by 30-32% and the compressive strength grows by 40-45%.

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Gaida Sedmale, Ģirts Stinkulis, Uldis Sedmalis, Inna Juhneviča, Jānis Kļaviņš. Illītu mālu raksturojums un pielietojums augst- un zemtemperatūras keramikas materiālu izstrādei

Divu veidu laboratorijas tehnoloģijas ir pētītas un pielietotas Latvijas Devona un Kvartāra ģeoloģisko periodu illītu mālu izmantošanai augst- un zemtemperatūras keramikas materiālu izstrādei. Tās ietver mālu ķīmisku apstrādi, pielietojot dažādas koncentrācijas Na vai K- sārmus ar sekojošu noteikta laika izturēšanu istabas vai 50-60^0C temperatūrā ar sekojošiem tradicionāli pielietotiem paraugu formēšanas, žāvēšanas un saķepināšanas procesiem. Pielietojot infrasarkano spektroskopiju, ir noteikts, ka, apstrādājot mālu sārmainā vidē, tiek izmainīta illītu dabīgā struktūra spektru daļā, kas norāda uz saišu O-Al-OH, kurā skābekļa jons ir saistīts ar blakus esošo Si-O kārtu, izmaiņām. Ir novērojamas arī izmaiņas, kuras, pēc autoru domām, saistāmas ar jaunu K-O-Si saišu izveidošanos un arī samērā ar pielietotā K- sārma koncentrācijas palielināšanos - ar jaunas Al-O saites veidošanos, AlO_4 grupā, kur Al – jons ir 4-koordinēts.Šīs mālu struktūras izmaiņas turpmākā saķepināšanas procesā ļauj pielietot temperatūru, kas ir par 200-250 ^{0}C zemāka par tradicionāli pielietoto, piemēram, būvkeramikai, 950-1000^0C intervālā, sasniedzot spiedes stiprību, kas ir adekvāta tradicioni saķepinātai keramikai un laboratorijas paraugiem, atrodas 15-22 MPa robežās.

Saistībā ar augst- un zemtemperatūras keramikas materiālu izstrādi, pielietojot Devona perioda illītu mālu 8-8.5 % kā saķepšanu veicinošu piedevu, ir noskaidrots, ka šī piedeva veicina saķepšanas procesu, kas rezultējas pētītās mullīta-ZrO_2 keramikas blīvuma un attiecīgi arī spiedes izturības pieaugumā. Šī piedeva veicina arī ZrO_2 tetragonālās modifikācijas veidošanos.

Гайда Седмале, Гиртс Стинкулис, Улдис Седмалис, Инна Юхневича, Янис Клявиньш. Характеристика иллитовых глин и их применение для разработки низко- и высокотемпературной керамики.

Исследованы лабораторные процессы по использованию Четвертичных и Девонских иллитовых глин Латвии для применения при разработке низко- и высокотемпературных керамических материалов. Первое включает обработку Четвертичных иллитовых глин Na или K-щелочью с выдержкой при комнатной или при температуре 50-60^0C в течение определенного времени с последующей формовкой образцов, сушкой и спеканием в интервале температур 100-600.700^0C. Применением инфракрасной спектроскопии установлено, что при химической обработке Четвертичной глины происходит изменение структуры иллитов в части спектра, которая указывает на изменение положения связей O-Al-OH, где кислород связан с рядом расположенным слоем Si-O. Наблюдаются также изменения относительно вновь образовавшихся связей K-O-Si и также с возрастанием концентрации K-щелочи образование новой связи Al-O, в группе AlO_4 где ион Al является 4-координированным. Эти структурные изменения позволяют снизить температуру обжига керамики на 200-250 ^{0}C по сравнению с традиционно применяемой в интервале 950-1000^0C и обеспечить прочность на сжатие в пределах 15-22 MPa.

В отношении высокотемпературной керамики следует отметить, что добавка 8-8.5 % иллитовой глины к исходной смеси муллито-ZrO_2 керамики значительно способствует процессу спекания и уплотнения этой керамики. Эта добавка снижает температуру образования муллита на 100 -150^0C, повышает прочность на сжатие и предотвращает переход ZrO_2 тетр в моноклинный в процессе охлаждения керамики.