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Effect of Delamination on Physico-Chemical Properties of Kaolin

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Abstract:

To provide the quality required for its use, raw kaolin must be subjected to certain processing procedures like delamination which is applied to the layered structure materials. The aim of this research is to determine the possibility of performing delamination in the extruder and to estimate the effects of this process on the physico-chemical properties of kaolin. The results showed that delamination can be efficiently realized in the extruder by shearing densely packed layers under the influence of friction force and added Na_2CO_3 electrolyte. The crystal structure of the system was thus disrupted. This was confirmed by the Hinckley index (HI) decrease and by the dilatometric characteristics changes during heating. The particle size was reduced and, furthermore, new adsorption centers were formed, which led to an increase in the total cation exchange capacity (CEC). The plasticity of kaolin decreased with the increasing delamination degree, as well as the amount of water required for plastic processing, which is favorable in drying ceramic products.

Keywords: Kaolin; Delamination; Hinckley index; Dilatometric properties; Plasticity.

1. Introduction

Clay is plastic semi-bound sediment formed by diagenesis (binding) of sludge-pelitic material (particle size below 0.005 mm) transported by water and precipitated in an aqueous environment. Besides, residual or sedimentary clays were formed and remained at the place of the primary material decomposition [1].

The composition of clay includes minerals that represent a large group of similar silicates. Among the silicates that are determined as clays, the most important crystalline representatives belonging to phyllosilicates are kaolinite, pyrophyllite, montmorillonite, illite, halloysite as well as amorphous allophane. Clay minerals are usually found in aggregates with one of them dominating. For instance, kaolinite clays are dominated by the mineral kaolinite.

Kaolinite is a hydrated aluminosilicate whose chemical formula is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The Si and Al ions in its crystal lattice are not interchanged but build alternate layers. The

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exchangeable cations are located only at the particles edges and do not penetrate into the interlayer space. The cation exchange capacity (CEC) of the kaolinite minerals group is relatively low and ranges from 2 to 10 mmol M⁺/100 g clay. Kaolinite crystallizes triclinically and has perfect cleavage along a base plane [2, 3]. The crystalline structure of kaolinite is formed by the condensation of one tetrahedral and one octahedral sheet.

The multi-layered kaolinite structure is formed by bonding tetrahedral and octahedral sheets. The layers are continually spread in the *a* and *b* direction of crystallographic axes in a way that the netting planes containing OH groups, t.e. the outer netting planes of the octahedral part of the layer, approach to oxygen netting planes, which are the bases of the tetrahedron from the neighboring kaolinite layer. Hydrogen from the OH group forms hydrogen bonds with oxygen from the adjacent layer. The layer as a whole has a permanent dipole character. The stacking of the layers in the *c* direction of the crystallographic axis can be: regular when the sheets are placed one above the other and can be moved parallelly in the *a* or *b* directions of the crystallographic axis, or spiral with a configuration corresponding to the coil stacking [4].

Hinckley introduced a method for measuring and determining the relative crystallinity, called the Hinckley index (HI) [5, 6]. A higher HI value means a larger probability for a more ordered crystal structure, while its lower value indicates a more defective structure and a more possible occurrence of two structural kaolinite forms mixture (low and high defective). The HI values are ranged from 0 for poorly to 1.6 for highly crystallized kaolinite.

The physico-chemical properties of kaolin are exceptionally important for its use [7-10]. Kaolinite is the main component of clays used as raw materials in the ceramics industry, but other present minerals also affect their properties. The content of clay minerals in ceramic masses is around 50 %. The most important properties of clay relevant for their further use are: chemical composition, plasticity, dilatometric properties, polymineral composition and crystal structure and cation exchange. As widespread mineral raw materials, clays find their application in many industries such as ceramic, paint, petroleum, bricks, paints and dyes, whereby their use is enormously growing [11-14].

Raw kaolin is usually used in the production of refractories. Before utilization in other industries, kaolin has to be processed to remove the impurities and to meet the quality requirements. This is especially important when performing a geologically-economic assessment of kaolin deposit [3].

One of the procedures for improving physico-chemical properties of the layered structure material is delamination, the process of separating laminas by cutting between the thinnest laminas and entering into the structure. It can be applied to kaolin owing to the layered structure of its main mineral kaolinite. By separation of the laminas, large flat kaolin plates with a high diameter/thickness ratio are formed. These delaminated kaolin plates positively affect ceramic extrusion properties, coated paper properties, and slip cast green strength [15-17]. The research revealed that physico-chemical properties of kaolin such as particle size distribution, CEC, plasticity, dilatometric and rheological properties are improved by delamination [18-20].

Delamination is conventionally performed by mechanical methods consisting of tumbling and stirred on vibratory media grinding on slurried or dried kaolin, whereby fracture of kaolin plates, followed by total destruction of kaolinite crystal structure occurs. The type of apparatus, media, and time determine the effect of the process. To minimize the fracture of kaolin plates, a chemical method, intercalation can be applied using urea, ammonium acetate, hydrazine, or potassium acetate which reversibly incorporates between the layers thus expanding the material before mechanical treatment [16].

The efficiency of kaolin delamination can be improved by adding electrolytes that charge kaolin particles thus accelerating the disruption of the crystal structure [21-24]. Also,

previous research reported examining changes in kaolinite induced by exposure to high pressure [25], chemical treatment [16], and mechanochemical treatment [26].

Taking into account the mentioned results, the idea in this study was to apply extrusion to achieve delamination of kaolin. The starting assumption was that due to the high friction degree occurring by spirally pushing a dense pulp towards the outlet of the extruder separation of the kaolin laminas can be expected. The effects of this extrusion on the physico-chemical properties of kaolin in terms of its future application were investigated. The following kaolin properties before and after extrusion were determined: moisture content, particle size distribution, CEC, dilatometric properties, plasticity, as well as the crystallinity level of kaolinite (HI). Also, the influence of Na_2CO_3 electrolyte addition in different concentrations was investigated.

2. Materials and Experimental Procedures

The tests were performed on kaolin concentrate samples obtained by processing of kaolinized granite from the "Garaši" deposit in the plant located at the mine.

Chemical analysis was carried out using the atomic absorption spectrophotometer (AAS), model AAnalyst 300, manufactured by "Perkin Elmer" and spectrophotometer; model Spekol 1300, produced by "JENA".

Moisture content was determined based on the masses of wet and dried sample.

X-ray powder diffraction (XRPD) analysis was realized to determine both the phase composition of the starting kaolin sample and the HI. For that purpose, a Philips diffractometer, model PW-1710, with a curved graphite monochromator and a scintillation counter was used. The intensities of diffracted $K\alpha$ X-ray radiation Cu ($\lambda = 1.54178 \text{ \AA}$) were measured at room temperature in the range of 2θ (θ diffraction angle) from 4 to 65° with the intervals of 0.02° , and periods of 2.5 s. The X-ray tube operates at the voltage of 40 kV and current of 30 mA, with slits for directing the primary and diffracted beam of 1° and 0.1 mm. JCPDS (Joint Committee on Powder Diffraction Standards) cards with numbers 9-0432 and 36-0426 were used to identify calcite minerals and dolomite minerals, respectively.

Kaolin preparations oriented and with parallel cleavage, were used to determine the HI. An amount of 150-180 mg of kaolin of particle size below $2 \mu\text{m}$ was mixed with $2\text{-}5 \text{ cm}^3$ of distilled water; then the dispersion was pipetted and dried on horizontal glass with an area of $45 \times 15 \text{ mm}^2$. The samples were treated with glycerin.

Particle size distribution was determined based on the different resistance of particles to moving in a fluid depending on their size on a cyclosizer NoM4, produced by "Warmen". The device consists of 5 cyclones of the same dimensions connected by nozzles of different diameters (63, 44, 33, 23, 15, and $11 \mu\text{m}$), which cause the different velocities of water movement in cyclones, thus obtaining six particle size classes.

Content of exchangeable cations (Ca^{2+} and Mg^{2+}) was determined by titration with 0.1 mol/dm^3 EDTA and a flame photometer "Dr. Lange Flammenphotometer M8D-Propane" by the calibration curve method (Na^+ and K^+) from the filtrate obtained by centrifugation of a solution of 1 g of a powdered sample in 100 cm^3 of $1 \text{ M NH}_4\text{Cl}$ at $\text{pH}=7$. The CEC was determined by titration of 0.3 g of powdered sample in 1 cm^3 of $5 \text{ N H}_2\text{SO}_4$ and 2 cm^3 of 4 % $\text{Na}_2\text{P}_4\text{O}_7$ by 0.3 % solution of methylene blue. The endpoint of the titration was recognized by the light blue ring around the dark blue drop which meant that the methylene blue was no longer adsorbed on the kaolin.

Delamination was performed using an extruder, type PZVM 86-HANDLE, which works on the principle of mechanical pushing of the sample between two spiral cylinders and by vacuum pulling towards the outlet (mouthpiece) with a square cross-section of 40 mm^2 . The kaolin samples were prepared with the moisture content adjusted to 25 % to achieve plasticity.

Delamination was realized on 3 series of samples:

- First series (U0), samples without any electrolyte added,
- Second series (U10), samples with 10 meq of Na₂CO₃/100 g sample, whereby this electrolyte amount approximately corresponds to the CEC of the investigated sample, valued to 7 meq/100 g sample,
- Third series (U20), samples with an excess of electrolyte added, in an amount of 20 meq of Na₂CO₃/100 g sample.

Sampling was carried out after 5, 10, 20, and 30 passes through the extruder. In the discussion that follows, the term delamination degree, indicating the number of extrusions through the device, is used.

Plasticity was determined by the Pfefferkorn method based on a flat head cylinder of known mass which falls from a certain height on cylindrical clay samples of different moisture content. Using these data, at investigated samples heights of 20 mm and 12.1 mm, the content of water for plastic processing and Pfefferkorn's plasticity index, respectively, were determined [27, 28].

Dilatometric tests were performed using a mechanical horizontal dilatometer "Linseis" where linear changes were transferred by a lever and thus registered. For the starting kaolin sample and the sample extruded for 30 times, dilatometric curves of linear deformation as a function of temperature were constructed.

3. Results and Discussion

3.1 Characterization of initial kaolin

3.1.1. Chemical composition

Chemical analysis of the initial kaolin sample (Table I) exhibited that oxides of Si and Al were predominant in kaolin with a content of 48.24 % and 33.93 %, respectively. The content of Fe oxide, with a value of 2.73 %, was slightly higher than the content of other oxides, which was negligibly low. The loss of ignition was ~12 %. Namely, chemically bound water is typical for materials with a layered structure, such as kaolin, so that water molecules incorporate between the octahedral and tetrahedral sheets of kaolinite, as the main mineral in kaolin, whereby the chemical bonds form.

Tab. I Chemical composition of the initial kaolin.

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	L.O.I.
Content, mass %	48.24	33.93	2.73	1.06	<0.10	0.082	1.60	12.01

3.1.2. Mineralogical composition

X-ray diffractogram of the initial powdered kaolin sample (Fig. 1) revealed that kaolin consisted of kaolinite, hydromica, quartz, muscovite, hydrobiotite, limonite, and rutile secondary minerals. Kaolinite is the most dominant mineral, and the most abundant accompanying component is mica.

3.1.3. Particle size distribution

The particle size distribution of the sample (Table II) showed that the class -11+0 μm predominated indicating fine-grained kaolin.

In Table II, $\sum M_{\downarrow}$ is the cumulative mass oversize (mass retained on the sieve) obtained by sequential addition of the masses from the first column starting from the top to bottom (as shown by the direction of the arrow), and $\sum M_{\uparrow}$ is the cumulative mass undersize

(mass passed through the sieve) obtained by sequential addition of the masses from the first column starting from the bottom to top (as shown by the direction of the arrow).

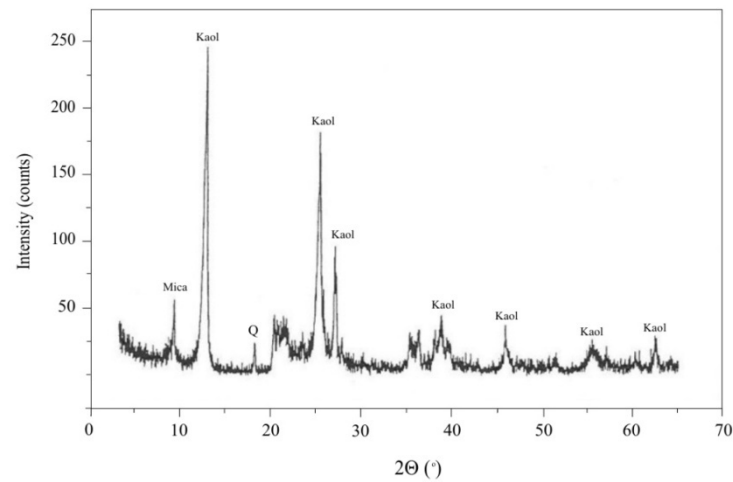


Fig. 1. XRPD pattern of initial kaolin (Kaol- kaolinite, Q- quartz).

Tab. II Particle size distribution of initial kaolin.

Class, μm	M, mass %	$\Sigma\text{M}\downarrow$, mass %	$\Sigma\text{M}\uparrow$, mass %
-63+44	1.83	1.83	100.00
-44+33	1.90	3.73	98.17
-33+23	2.80	6.53	96.27
-23+15	6.84	13.37	93.47
-15+11	9.16	22.53	86.63
-11+0	77.47	100.00	77.47
Passing	100.00		

3.1.4. Cation exchange capacity

The type and content of exchangeable kaolin cations were determined by the ion exchange method with 1M NH_4Cl , and the total CEC (ΣCEC) was calculated as the sum of the concentrations of exchangeable cations.

Tab. III Type and content of exchangeable cations.

CEC, meq/100 g	Kaolin
Ca^{2+} and Mg^{2+}	5.60
Na^+	0.40
K^+	0.30
ΣCEC	6.30
Ka(MB) , mg/g	25.00
CEC from Ka(MB) , meq/100g	7.80

The results of the type and content of exchangeable cations (Table III) revealed that the total CEC was 6.30 meq/100 g sample, while calculated using the adsorption coefficient of methylene blue (Ka(MB)) reached 7.80 meq/100 g sample. This difference can be explained by the fact that owing to the large specific surface area of kaolin, the Ka(MB) value was high (25 mg/g), and thus the calculated CEC.

3.2 Characterization of delaminated kaolin

Physico-chemical properties, important for the kaolin further use, were monitored after 5, 10, 20, and 30 passes through the extruder of all three samples series prepared for delamination- U0 (without electrolyte), U10 (with 10 meq of Na₂CO₃/100 g sample added), and U20 (with 20 meq of Na₂CO₃/100 g sample added).

3.2.1. Impact of delamination on moisture content

The obtained results of the moisture content for the delaminated kaolin (Table IV) revealed that with the increasing number of extrusions, the moisture content of all three series decreased. With the enhancing delamination degree, both the device and the sample were heating up which resulted in losing the present moisture by evaporation. The high friction degree between the sample and the inside walls of the extruder caused the temperature increase. Furthermore, the sample exited through the mouthpiece of the extruder due to the spiral pushing, so that a high friction degree and additional heating of the sample also occurred at that place.

Tab. IV Moisture content in delaminated kaolin.

Number of extrusions	Moisture content, mass %		
	U0	U10	U20
0	25.81	26.96	25.83
5	25.31	26.69	25.31
10	24.65	26.25	24.68
20	23.34	25.60	23.17
30	21.83	25.11	22.39

Based on the results in Table IV, it can be concluded that in all three series the decrease of moisture content after 5 and 10 extrusions is very small (< 5 % for U0 and U20 and < 3 % for U10) and becomes more significant after 20, and especially after 30 extrusions.

Comparing the series U0 and U20, it is evident that the values of moisture content are practically the same for 0,5 and 10 extrusions; very small differences between the series occur only after 20 and 30 extrusions, so it can be said that they have approximately the same moisture content drop (15.42 % for U0 and 13.31 % for U20).

However, the decrease in the moisture content of the U10 series, after 5 and 10 extrusions, as well as after a larger number of extrusions is significantly lower compared to the U0 and U20 series and reaches 6.86 % after 30 extrusions. Namely, the amount of 10 meq Na₂CO₃/100 g sample is optimal, while with 20 meq Na₂CO₃/100 g of sample the excess electrolyte is introduced, whereby its influence does not exist, i.e. the sample behaves like U0.

3.2.2. Impact of delamination on particle size distribution

Having in mind that fine-grained kaolin was used, the predominant class -11+0 μm (Table II) was monitored in all three series of experiments to determine whether the delamination degree and added electrolyte affected its content.

According to the obtained results of content of class -11+0 μm in delaminated kaolin (Table V), in the first series, U0, the content of class -11+0 μm was uniform until the tenth extrusion and ranged from 79.91 % to 81.83 %. After twenty and thirty extrusions, the content of that class increased to 84.23 % and 84.49 %, respectively, which is not a significant difference. In the second series, U10, a rapid increase in the smallest class is noticed at the very beginning of the delamination process. After the fifth pass through the extruder, the

content of class $-11+0 \mu\text{m}$ increased from 78.24 % to 84.00 %. With further delamination, the share of this class continued to increase, but not significantly like at the beginning, and eventually reached 86.31 %. In the third series, U20, until the tenth extrusion, the increase in the content of class $-11+0 \mu\text{m}$ was significant, from 78.37 % to 85.54 %. After the twentieth and thirtieth pass, a slight rise to 86.00 % and 86.70 %, respectively, is evident.

Tab. V Content of class $-11+0 \mu\text{m}$ in delaminated kaolin.

Number of extrusions	Content of class $-11+0 \mu\text{m}$, mass %		
	U0	U10	U20
0	79.91	78.24	78.37
5	81.53	84.00	83.98
10	81.83	84.10	85.54
20	84.23	86.26	86.00
30	84.49	86.31	86.70

The results showed that in all three series, with the rising number of extrusions, the content of class $-11+0 \mu\text{m}$ was increasing. This indicates that the sample was additionally grinded by delamination. Also, grinding the sample is more pronounced in series with the electrolyte added. The present electrolyte charges the kaolinite particles, thus accelerating the delamination process and emphasizing the imbalance of the internal structure, which resulted in reducing the particle size of the sample to a level that corresponded to the dimensions of the kaolinite laminas. By adsorption of cations from electrolytes, the surfaces of kaolinite particles became positive and mutually repel, thus contributing to faster dispersion during delamination.

The amount of added electrolyte did not greatly influence the increase of the observed size class content. This can be explained by the fact that an optimal electrolyte concentration caused positive effects, which was, in this case, a concentration of 10 meq $\text{Na}_2\text{CO}_3/100 \text{ g}$ samples corresponding to the CEC value of kaolin.

3.2.3. Impact of delamination on CEC

The influence of delamination on CEC was analyzed by monitoring the values of total CEC determined based on exchangeable cations ($\sum\text{CEC}$), adsorption coefficient of methylene blue ($K_a(\text{MB})$), and CEC calculated based on the adsorption of methylene blue in delaminated kaolin samples for all three series.

The obtained results (Table VI) revealed that with the increasing number of extrusions of the first samples series (U0), the $\sum\text{CEC}$ slightly increased. CEC calculated based on the $K_a(\text{MB})$ enhanced with the increasing delamination degree from 7.50 to 9.70 meq/100 g. This pointed out that due to grinding during the delamination process; new active adsorption centers on the surface of kaolinite particles were formed. In such a way, the conditions for increasing the adsorption degree arose, which resulted in CEC increase [29].

The $K_a(\text{MB})$ increased from 24 mg/g for a non-delaminated sample to 31 mg/g for the sample after 30 passes through the extruder.

With an increasing delamination degree for the sample of the second series (U10), changes in the $\sum\text{CEC}$ values were almost insignificant. The CEC values determined based on $K_a(\text{MB})$ increased from 8.13 meq/100 g sample for the non-delaminated sample to 10.00 meq/100 g for the sample after 30 extrusions. The $K_a(\text{MB})$ also increased with the increasing number of extrusions from 26 to 32 mg/g.

For the sample U20, with an increasing delamination degree, the $\sum\text{CEC}$ increased from 7.58 to 12.10 meq/100 g sample. Also, the CEC determined using $K_a(\text{MB})$ increased from 8.44 to 9.69 meq/100 g sample and the $K_a(\text{MB})$ from 27 to 31 mg/g. The enhancement

in CEC occurred due to the sample grinding during the delamination, which was confirmed by the change in the particle size distribution, and by the creation of adsorption centers.

Tab. VI Total CEC, Ka(MB), and CEC from Ka(MB) in delaminated kaolin.

Number of extrusions	Series	Σ CEC, meq/100 g	Ka(MB), mg/g	CEC from Ka(MB), meq/100g
0	U0	6.80	24.00	7.50
	U10	6.57	26.00	8.13
	U20	7.58	27.00	8.44
5	U0	7.40	26.00	8.10
	U10	6.86	27.00	8.44
	U20	9.10	31.00	9.69
10	U0	7.79	28.00	8.80
	U10	7.17	27.00	8.44
	U20	9.50	31.00	9.69
20	U0	7.25	28.00	8.80
	U10	6.56	30.00	9.38
	U20	9.00	30.00	9.38
30	U0	7.69	31.00	9.70
	U10	7.05	32.00	10.00
	U20	12.10	31.00	9.69

Generally, the delamination caused an increase in CEC of all samples. Enhancement of CEC, however, as well as of the Ka(MB) was greater for the sample with electrolyte compared to the sample without electrolyte. As already pointed out, the electrolyte intensified the effect of delamination that grinded the sample to a particle size of 10 μm thus creating new adsorption centers. Also, the sample with a higher electrolyte concentration, U20, for the same number of extrusions generally exhibited higher values of the CEC and the Ka(MB) compared to the sample with a lower content of electrolyte, U10.

3.2.4. Impact of delamination on plasticity

The change in the water content necessary for plastic processing (WPP) and the Pfefferkorn's plasticity index (PPI) were monitored with the aim to establish how the delamination process during the extrusion of the sample affected the kaolin plasticity. These two physical quantities were determined for all three series, on the non-delaminated samples and on the samples extruded for 30 times.

According to the results in Table VII, WPP for the sample U0 decreased from 40.30% in the non-delaminated sample to 37.75 % in the sample after 30 extrusions and PPI values from 45.65 % to 42.90 % for the same samples. The decreasing trend for WPP and PPI was also observed in the sample U10. Hence, WPP decreased by delamination from 40.20 % to

35.25 % and PPI from 45.05 % to 40.45 %. In the case of a sample containing an excess of electrolyte (U20), the values of WPP and PPI were also reduced from 40.95% to 34.20% and from 44.85 % to 40.30 %, respectively.

Tab. VII Water content for plastic processing (WPP) and the Pfefferkorn's plasticity index (PPI).

Number of extrusions	Series	WPP, %	PPI, %
0	U0	40.30	45.65
	U10	40.20	45.05
	U20	40.95	44.85
30	U0	37.75	42.90
	U10	35.25	40.45
	U20	34.20	40.30

Generally, delamination reduced the consumption of water for plastic processing, which was favorable from a practical point of view. The water amount decrease after 30 extrusions of the samples U10 and U20 was on average 14 % and for the sample U0 was about 6 %, which was a pronounced positive effect from the energy point of view. Namely, less water required for plastic processing meant lower energy consumption in the drying process of ceramic products obtained from the tested kaolin. Evidently, the reduction of WPP and PPI by delamination was greater in the samples with electrolyte compared to those without electrolyte. The lowest WPP was for the sample U20 after 30 extrusions but the sample U10 exhibited practically the same WPP.

For better understanding the plasticity change, the definition saying that plasticity is a property that designates the behavior of kaolin when mixed with water is useful. Kaolin shows plasticity in a very narrow range of water content and for most types it is from 15 to 25 %. For this water content, a very fine membrane is formed around the kaolin particles, which provides plasticity [3]. Plasticity is related to the degree of particle packing in the kaolin structure [28]. Kaolins with densely packed particles in the structure exhibit higher plasticity. The explanation of why delamination reduced the kaolin plasticity was given on that basis. Delamination enhanced the interbase distance between the kaolin layers and thus reduced the density of its packaging, which led to a plasticity decrease. Plasticity also depends on the specific surface area of kaolin- a larger specific surface area implies greater plasticity. Regardless of the fact that the sample is grinded by delamination thus increasing its specific surface area, the plasticity decreased, because a decrease in the packing density had a greater impact on plasticity than the specific surface area. As already pointed out, the delamination effect on the plasticity decrease was more pronounced for the samples with electrolytes. The reason for that lies in the fact that Na_2CO_3 charged kaolin particles that repel each other, which supported delamination and reduced the degree of the particles packing. Also, by the addition of this salt, the monovalent Na^+ ions are bonded to the surface of kaolin particles, which resulted in bonding less water to the kaolin structure, and therefore its plasticity was lower. Tests showed that cations of lower charge bonded less water.

3.2.5. Impact of delamination on dilatometric characteristics and Hinckley index

Dilatometric tests were carried out with the aim to reveal how kaolin behaved during continuous heating, i.e. to determine temperatures when changes in its structure occurred. This is very important for establishing the firing conditions.

Dilatograms are typical for kaolin minerals, and the difference indicates structure changes caused by delamination.

Dilatograms of the initial kaolin sample and the delaminated sample extruded for 30 times (Fig. 2) revealed that the structure changes of the delaminated sample occurred a bit earlier than the changes in the initial sample. This was a consequence of the imbalance in the kaolin structure caused by delamination, which resulted in the appearance of dimensional variations at lower temperatures.

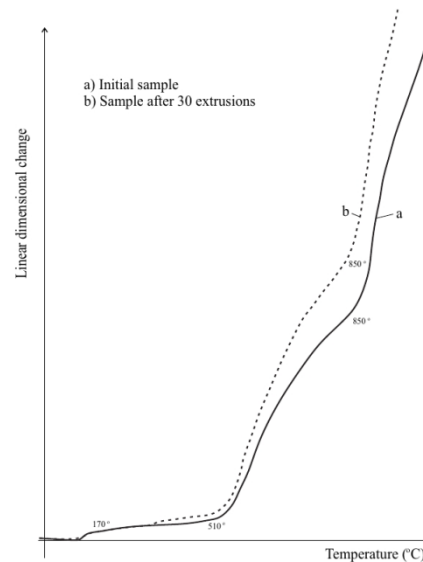


Fig. 2. Kaolin dilatograms.

Beside the different dilatometric characteristics of the initial and delaminated kaolin samples, indicating structure changes induced by delamination, the evidence of these changes were the different HI values before and after extrusions, registered by X-ray analysis.

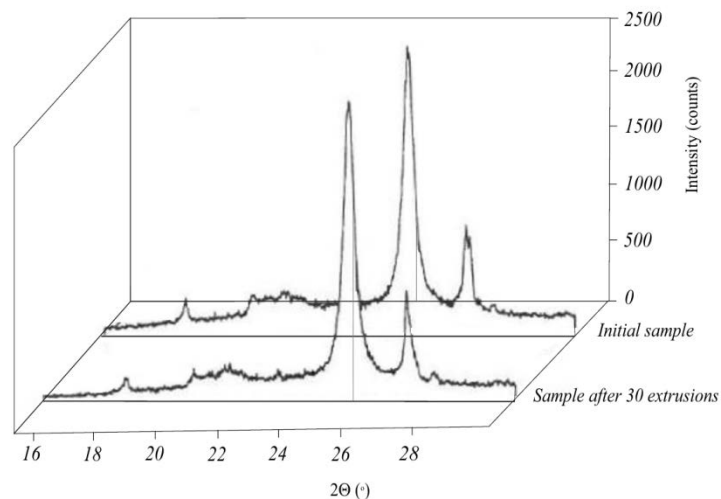


Fig. 3. Kaolin diffractograms before and after delamination.

Comparative diffractograms of the initial and delaminated kaolin samples (Fig. 3) pointed out to the difference in width and sharpness of reflections. The data obtained according to the Hinckley method [5] were read from the diffractograms. The calculated HI values for the initial and delaminated samples were 0.50 and 0.47, respectively; different

values indicated differences in the crystallinity level, i.e. different degrees of structural order. A higher HI value meant a higher crystallinity level and a higher internal order of the system. The lower HI value of the delaminated kaolin sample confirmed the claim that the delamination process induced structural changes inside kaolin and disturbance of the internal order of the system [30].

The delamination process caused translational movement of the kaolinite layers in the direction of one of the crystallographic axes, a or b , which resulted in the crystallinity level decrease, t.e. in the HI. By delamination, large kaolinite aggregates were separated by shear to form plenty of thin plates with a big diameter [31], Fig. 4.

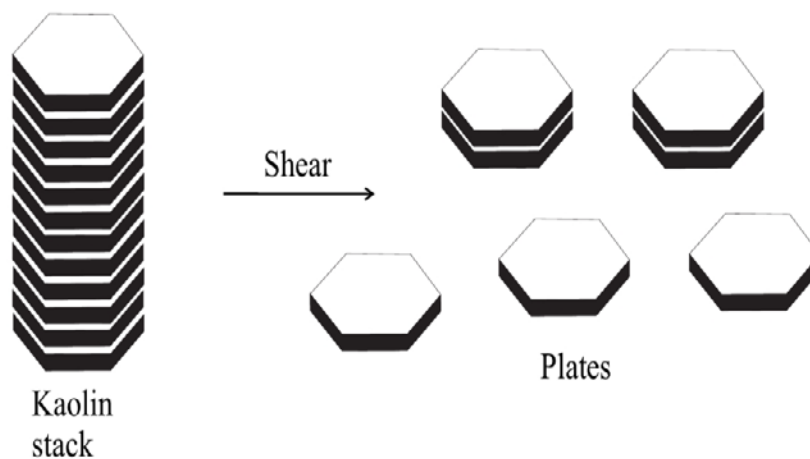


Fig. 4. Schematic diagram of delamination process [31].

3.3 Mechanism of delamination-induced changes in the kaolinite crystal structure

Based on the monitored changes in physico-chemical quantities on the initial and delaminated kaolin samples, the mechanism of delamination action on the change in the kaolinite crystal structure was assumed. The decrease of the HI value in the delaminated sample in relation to the initial one indicated that the partial destruction of the kaolinite crystal structure and its partial amorphization took place [26, 32]. Having in mind that kaolin was ground by this process, the conclusion can be drawn that the delamination mechanism was approximately the same as the grinding mechanism [26, 30, 33, 34].

Owing to the high friction degree, the hydrogen bonds between the kaolinite layers were destroyed causing their differentiation and decrease in the strength of the bonds Si-O and Al-OH at the edges as well as the formation of particles with a curved surface. The tetrahedral sheet remained unchanged, while the octahedral one was disturbed resulting in occurrence of series of structurally deformed $\text{Al}(\text{O},\text{OH})_4$ octahedral sheets and residual tetrahedral SiO_4 sheets. OH groups were released, external much faster than internal, and by their interaction, water bonded to a highly active surface as coordinated water, was formed. Water from the atmosphere hydrated the kaolinite surface which also affected its properties.

4. Conclusion

Delamination of kaolin, obtained by processing of kaolinized granite from the "Garaši" deposit, was carried out in an extruder on a pure sample and on samples with an

electrolyte content of 10 meq Na₂CO₃/100 g sample and 20 meq Na₂CO₃/100 g sample. Based on the presented results, the following can be concluded:

1. The effects of the delamination were more pronounced in samples with an electrolyte. By adsorbing Na⁺ ions from the electrolyte, kaolin particles became positive, mutually repelled and supported delamination of densely packed kaolin layers.
2. Owing to the high friction degree with increasing the delamination degree, the samples were heated and the moisture content decreased.
3. Monitoring the content of class -11+0 μm pointed out that the sample was additionally ground during the delamination process, especially in the presence of electrolyte. The amount of added electrolyte, however, did not have a significant impact on increasing the content of the observed size class. This is explained by the fact that the electrolyte had an optimal concentration which induced positive effects. In this case, this concentration was 10 meq Na₂CO₃/100 g of sample, which corresponded to the CEC value of kaolin.
4. The CEC as well as the adsorption coefficient increased with the increasing delamination degree.
5. With the increasing delamination degree, the consumption of water for plastic processing of kaolin decreased.
6. Based on different dilatometric characteristics of the initial and delaminated kaolin samples, the conclusion was drawn that the delamination procedure reduced the internal order of the system resulting in the occurrence of dimensional changes in the delaminated sample at lower temperatures.
7. Extrusion can be successfully applied to layered structure materials, such as kaolin, whereby delamination and enhancement of certain physico-chemical properties essential for its use occurred. This was proved by reducing the HI value of delaminated kaolin as a measure of the internal order of a system having a crystalline structure.
8. In terms of practical application, the benefits can be seen in energy savings when drying ceramic products based on delaminated kaolin owing to its lower water consumption for plastic processing; higher CEC and adsorption coefficient make delaminated kaolin better adsorbent compared to nonlaminated.

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Сажетак: Да би се обезбедио квалитет потребан за употребу, сирови каолин мора бити подвргнут одређеним поступцима обраде попут деламинације која се примењује код материјала слојевите структуре. Циљ овог истраживања је да се утврди могућност извођења деламинације у екструдеру и процене ефекти овог процеса на физичко-хемијска својства каолина. Резултати су показали да се деламинација може ефикасно извршити у екструдеру смицањем густо пакованих слојева под дејством силе трења и додатог електролита Na_2CO_3 . На тај начин нарушена је кристална структура система. То је потврђено смањењем Хинклијевог индекса и променама дилатометријских својстава током загревања. Величина честица је смањена и, надаље, формирану су нови адсорпциони центри, што је довело до повећања укупног

капацитета катјонске измене. Пластичност каолина смањује се са порастом степена деламинације, као и утросак воде за пластичну обраду, што је повољно у процесу сушења керамичких производа.

Кључне речи: каолин, деламинација, Хинклијев индекс, дилатометријска својства, пластичност.

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