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STUDY OF MINERALOGICAL CHANGES IN SMEDERVESKA PALANKA BRICK CLAY DEPENDING ON FIRING TEMPERATURE

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Abstract

In this paper authors consider changes of mineralogical composition depending on firing temperature of Smederevska Palanka brick clay. Research of the influence of firing temperature on mineralogical composition was performed on fraction samples with particle size up to 5μm of studied clay and subjected to thermal treatment at temperature of 600°C, 800°C, 1000°C and 1200°C. The samples were then subjected to x-ray diffraction analysis (XRD) and to examinations by scanning electron microscopy (SEM).

It was found that during firing Smederevska Palanka brick clay had the characteristic to develop mineralogical phases of hematite, melilite, monticellite, wollastonite and mullite. In this clay the decrease of porosity by increase of firing temperature was found as well as some presence of glassy phase which also was proportional to the increase of firing temperature.

Key words: *Brick clay, firing temperature, X-ray diffraction analysis, Scanning electron microscopy, mineralogical phase.*

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1. Introduction

Smederevska Palanka Brick Clay is the basic component in composing of brick mass for production of brick products in Brick Company in Smederevska Palanka. Clay is obtained by surface exploitation. The particles up to 5 µm are obtained by decantation method from the pit raw materials, in order to concentrate clay minerals.

After appropriate preparation, this fraction is subjected to x-ray difraction examination (XRD) as well as to examinations by scanning electron microscopy (SEM) with the aim to establish mineral phase caused at various firing temperature.

2. Experimental

Chemical composition of starting raw materials has been determined by regular chemical analysis and it is presented on Table 1. and during this chemical analysis of pit clay raw material the fraction ≤5µm has been performed as well.

Table 1. Chemical composition of Smederevska Palanka brick clay: the pit raw material and its fraction ≤5 µm

Component (%)	Smederevska Palanka brick clay	
	Pit raw material	Fraction ≤5µm
SiO_2	62,82	47,76
TiO_2	0,87	0,62
Al_2O_3	13,58	18,92
Fe_2O_3	4,43	6,44
CaO	6,26	5,17
MgO	1,30	1,57
Na_2O	0,79	0,56
K_2O	2,15	2,56
loss by burning	7,74	16,43
total	99,94	100,03

Study of fired samples by x-ray difraction (XRD) method and scanning electron microscopy (SEM) of fraction ≤5µm of the tested sample included x-ray with the aim to establish the changes of phased i.e. mineral composition. Samples of the tested clay in form of testing bodies prepared of 5µm fraction were subjected to thermal treatment at temperatures of 600°C, 800°C, 1000°C and 1200°C (in laboratory oven with the firing cycle of 24 hours and keeping 1 hour at maximum temperature), after which they were prepared by crushing for x-ray. X-ray difraction analysis was performed on Phillips PW1710 diffractometer with filtered Cu radiation (40 kV, 30 mA) in the angular range of 4-60°. Study of fired samples by usage of Philips 2433 scanning electron microscopy was also performed.

3. Results and discussion

Considering the chemical composition of pit clay sample and fraction ≤5µm, it was noticed that reduction of SiO_2 was made in the sample, which is the consequence of considerably reduced share of content of free quartz in the fraction, in comparison with the pit sample, while the share of carbonate is still considerable in proportion to its content in the sample in the pit condition. The content of Al_2O_3 in ≤5µm fraction is considerably increased, which is result of increased content of clay mineral in it. Also, the loss by burning is more considerable.

XRD diagram of ≤5(µm) fraction sample of brick clay from Smederevska Palanka fired at 600^0C is shown on Figure 1, while the image made by scanning electron microscopy of ≤5(µm) fraction sample of brick clay from Smederevska Palanka fired at 600^0C is shown on Figure 2.

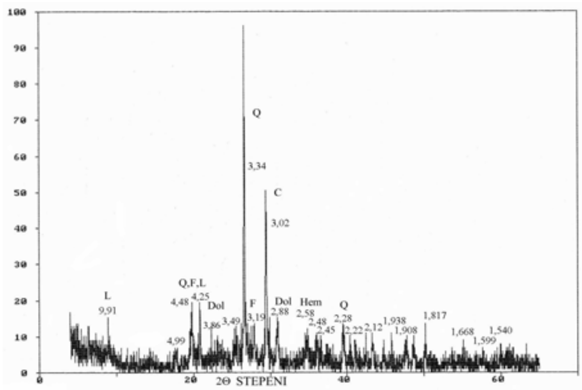

Fig. 1. XRD diagram of ≤5µm fraction sample of brick clay fired at 600^0C.

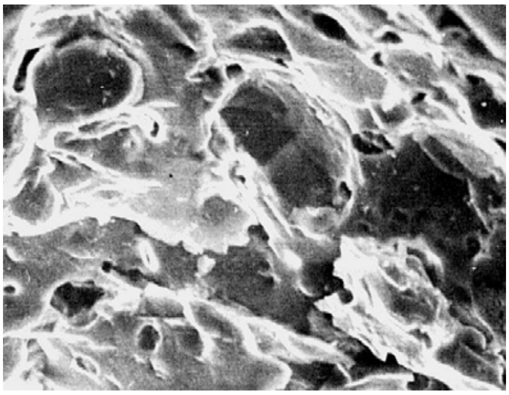

Fig. 2. SEM-image ≤5μm fraction sample of clay fired at 600^0C, Magnification 2000x.

XRD image of the fraction sample of ≤5μm brick clay from Smederevska Palanka at 600^0C shows complete dehydration of kaolinite and hydromica phase, while the other minerals are practically unchanged. Mica that has been partly transformed into hydromica phase has also suffered certain changes, as hydromicas are dehydrated, which is manifested by reduction of basal inter-atom distance. Hematites were formed at this temperature as a new phase, by dehydration of iron hydroxide, and except for hematite no other phases have been formed.

The image on scanning electron microscope of fraction sample of ≤5μm brick clay from Smederevska Palanka fired at 600^0C (Figure 2) shows that large pores were formed as result of dehydration of kaolinite and smectite phase as well as inter-layer phylosilicate. It is noticeable at SEM-image that dehydration process, especially of smectite phase in terms of texture, given spheric shapes with considerable presence of pores. Amorphous products of dehydration made of aluminosilicate complexes appear on the edge of spheric dehydrated smectite aggregates.

XRD diagram of ≤5μm fraction sample of brick clay from Smederevska Palanka fired at 800^0C is shown on Figure 3, while the image made by scanning electronic microscopy of ≤5μm fraction sample of brick clay from Smederevska Palanka fired at 800^0C is shown on Figure 4.

XRD diagram of fraction sample of ≤5μm brick clay from Smederevska Palanka fired at 800^0C is considerably different from x-ray diagram that refers to previous temperature, especially in terms of presence of some newly formed phases. It is noticed that monticellite and melilite (Mt, Me) are formed as a result of reaction of amorphous aluminosilicate complex with calcium and magnesium. Micas take normal basal reflections, which is the sign that complete dehydration of newly formed phases has taken place on them, especially smectite and hydromica.

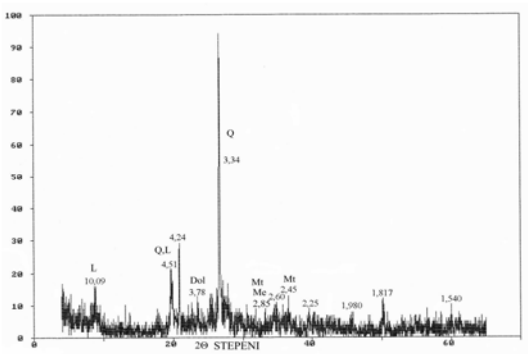

Fig. 3. XRD diagram of ≤5 μm fraction sample of brick clay fired at 800^0C.

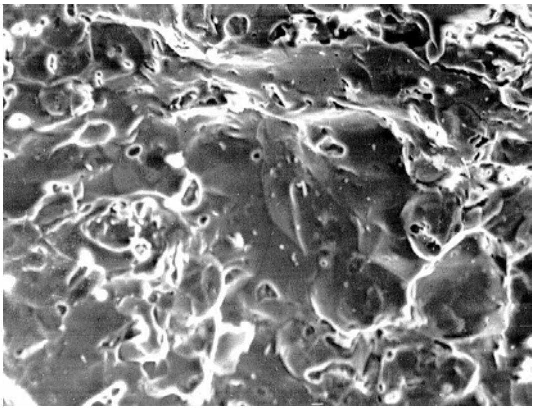

Fig. 4. SEM-image ≤5μm fraction sample of brick clay fired at 800^0C, Magnification 2000x.

SEM-image of fraction sample of ≤5μm brick clay from Smederevska Palanka fired at 800^0C (Figure 4) differs from previous SEM-image according to clearly noticeable new phases which are stated and x-ray way, as well as by reduced porosity degree. Presence of somewhat higher content of glassy phase is noticed at this temperature.

XRD diagram of ≤5μm fraction sample of brick clay from Smederevska Palanka fired at 1000^0C is shown on Figure 5, while the image made by scanning electronic microscopy of ≤5μm fraction sample of brick clay from Smederevska Palanka fired at 1000^0C is shown on Figure 6.

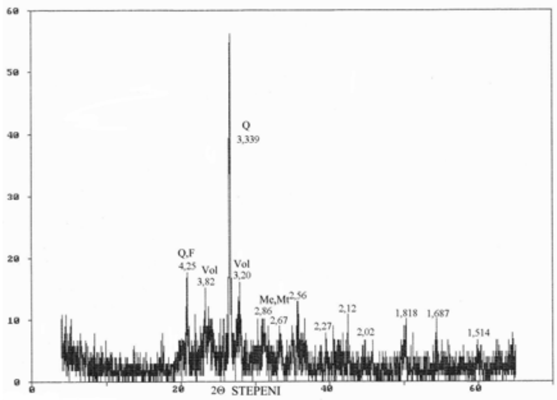

Fig. 5. XRD diagram of ≤5μm fraction sample of brick clay fired at 1000^0C.

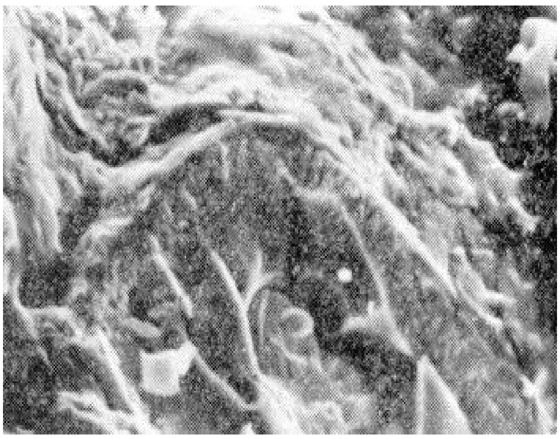

Fig. 6. SEM- image ≤5μm fraction sample of brick clay fired at 1000^0C. Magnification 2000x

XRD diagram of this sample fired at temperature of 1000^0 C is featured by complete dissociation of carbonate of calcite type as well as mica, where Ca from calcite with amorphous silicium complexes and partly

quartz Q gave wollastonite as a new phase which was not formed at previous firing temperature of this sample (800^0C). At this diagram, reduction of intensity of peak for quartz (Q) is noticed, as its reduction took place in reaction with dislocated Ca from calcite and formation of wollastonite. The sample from Smederevska
Palanka is rich in content of calcite and other carbonates of dolomite type and at this temperature complete dissociation of dolomite, with appearance of phases of melilite and monticellite type took place.

SEM-image of reaction sample of ≤5μm brick clay from Smederevska Palanka fired at 1000^0C, which is shown on Figure 6, shows the mixture of wollastonite with melilite and monticellite. In this fraction sample of ≤5μm brick clay from Smederevska Palanka fired at 1000^0C, degree of porosity at this temperature was lower with the same sample prepared by firing at previous temperature (800^0C).

XRD diagram of ≤5μm fraction sample of brick clay from Smederevska Palanka fired at 1200^0C is shown on Figure 7, while the image made by scanning electronic microscopy of ≤5μm fraction sample of brick clay from Smederevska Palanka fired at 1200^0C is shown on Figure 8.

XRD diagram of the sample fired at temperature of 1200^0 C (Figure 7) shows presence of lower quantities of mullite as a newly formed phase which was made at this temperature. Presence of wollastonite (Vol), melilite (Me), monticellite (Mt) and quartz (Q) is kept.

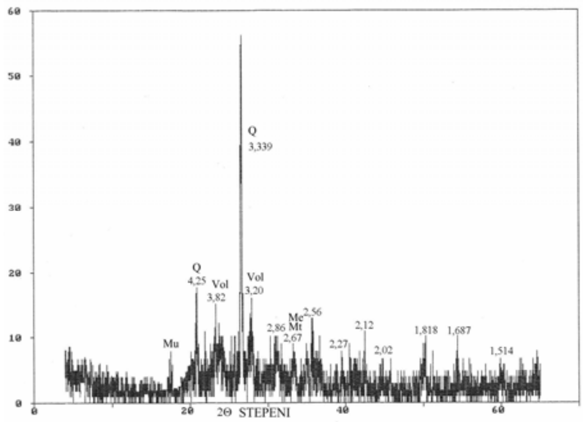

Fig. 7. XRD diagram of ≤5μm fraction sample of brick clay fired at 1200^0C.

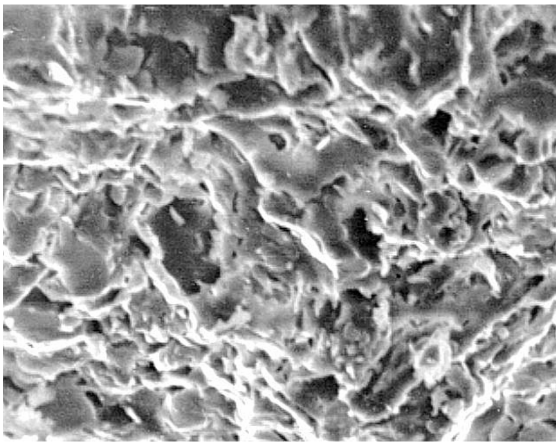

Fig. 8. SEM- image ≤5μm fraction sample of brick clay fired at 1200^0C. Magnification 2000x.   .

At SEM-image of fraction sample of ≤5μm brick clay from Smederevska Palanka fired at 1200^0C, which is shown in Figure 8, somewhat larger aggregates of wollastonite, melilite, monticellite as well as mullite are noticed. Melilite aggregates are larger than monticellite aggregates and they show tendency of forming more regular needle-shaped or needle-shaped – pole-like aggregates. By observation on the electron microscope, rounded forms of quartz grain can be seen, where presence of melilite and monticellite aggregate appears on the edge. Porosity is lower than in the sample fired at 1000^0C, and formed pores are partly filled with glassy phase. In the basic body, which is glassy, crystallisation centres are noticed to minor extent; crystallisation centres pertain to melilite, i.e. monticellite type, while crystallisation centres with mullite are less frequent.

4. Conclusion

Brick clay from Smederevska Palanka at firing temperature of 600^0C is featured with complete dehydration of kaolinite and hydromica phases, and dehydration of smectites phase is noticed, which gives spheric shapes with considerable porosity of texture structure, so that porosity of high degree is noticed. With this sample, as the consequence of Fe hydroxide dehydration, hematite appears as a new phase.

In fraction sample of ≤5μm brick clay from Smederevska Palanka fired at temperature of 800^0C, formation of monticellite and melilite is noticed, unlike the samples of the same raw material fired at previous temperature, as result of reaction of amorphous aluminosilicate complex with calcium and magnesium. Somewhat lower degree of porosity can be noticed here as compared to previous one and appearance of liquid phase is stated.

By studying the fraction sample of ≤5μm clay from Smederevska Palanka fired at temperature of 1000^0C, it is noticed that complete dissociation of carbonate, calcite and dolomite, as well as mica took place, so that amorphous aluminosilicate complex in reaction with quartz and calcium formed the new phase at this temperature, wollastonite. Somewhat higher content of melilite and monticellite as well as of glassy phase is noticed, while the degree of porosity is lower as compared with the noticed one in the samples of the same raw materials fired at previous temperature.

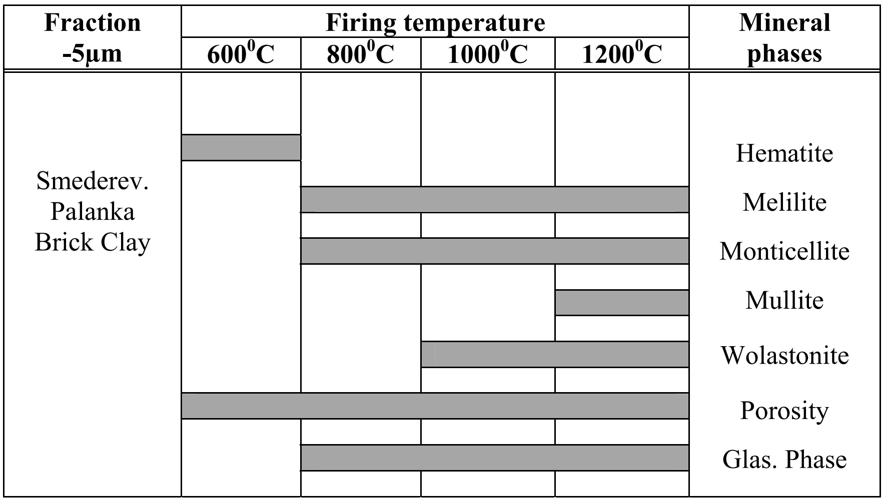

Fig. 9. Survey of mineral phase depending on firing temperature of ≤5μm fraction sample of Smederevska Palanka brick clay (indicative).

At firing temperature of 1200^0C, aggregates of wollastonite, melilite, monticellite as well as mullite which appear as newly-formed phase are noticed. Please note that in this sample of brick clay from Smederevska

Palanka, content of mullite is considerably lower as compared to previous samples prepared of other raw materials and fired at this temperature. Melilite aggregates are larger than monticellite aggregates and they show tendency of forming needle-shaped and pole-like aggregates. Porosity of matrix is still noticeable and formed pores are partly filled with glassy phase.

The Figure 9 gives illustration indicative of mineral phases, depending on the firing temperature, of ≤5µm fraction sample of Smederevska Palanka brick clay.

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