

MINERALOGICAL CHANGES IN ZORKA BRICK CLAY DEPENDING ON FIRING TEMPERATURE

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Abstract

The paper considers changes of mineralogical composition depending on firing temperature of Zorka brick clay. Research of the influence of firing temperature on mineralogical composition was performed on fraction samples with particle size up to 5 μ m 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 (RDA) and to examinations by scanning electron microscopy (SEM).

Zorka brick clay at firing temperature of 600 °C shows presence of distinct porosity with clay mineral dehydration process as well as formation of Hematite as a new phase due to present iron hydroxide, while mica remains untransformed at this temperature. At temperature of 800 °C, rounding of grain borders takes place and mica phase into the basic mass which is made of transformed amorphous clay minerals. At 1000 °C, appearance of Melilite can be noticed, while reduction of mica quantity is noticeable due to hydration at this temperature. It can be also stated here that porosity with appearance of glassy phase is present here. At firing temperature of 1200 °C, presence of glassy phase which fills space within the present Mullite and Melilite aggregate is noticeable. Presence of Hematite is also noticed here, as well as presence of relict remaining of feldspar. Porosity still exists, but at lower level compared to the one stated during the study of sample from the same raw material fired at previous

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temperature, which is consequence of considerably more distinct presence of glassy phase in this case.

It was found that during firing Zorka brick clay had the characteristic to develop mineralogical phases of Hematite, Melilite 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.

Keywords: *Brick clay, Firing temperature, Porosity, Glassy phase, Mineralogical phase, RDA diagram, Scanning electron microscopy.*

1. Introduction

Zorka brick clay is the basic component in composing of brick mass for production of brick products in company Zorka Nemetali a.d. in Sabac. Clay is obtained by surface exploitation (Figure 1). The particles up to 5 μm are obtained by decantation method from the pit raw materials, in order to concentrate clay minerals.



Fig. 1. Surface excavation site of Zorka brick clay Sabac

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

2. Chemical composition of starting raw materials

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 - 5 μ m has been performed as well. Also, the composition of quartz by standard chemical method was determined for the pit clay raw material.

Considering the chemical composition of pit clay sample and fraction - 5 μ m, it was noticed that reduction of SiO₂ 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 Al₂O₃ in -5 μ m fraction is considerably increased, which is result of increased content of clay mineral in it. On the other hand, increased content of K₂O is noticed in this fraction, which is consequence of increased content of hydro-mica component in this sample. Also, the loss by burning is more considerable.

Table 1. Chemical composition of pit raw material and its fraction -5 μ m

Component (%)	Zorka brick clay	
	Pit raw material	Fraction -5 μ m
SiO ₂	67,13	49,66
TiO ₂	0,81	0,61
Al ₂ O ₃	18,36	29,10
Fe ₂ O ₃	4,49	1,82
CaO	0,47	3,39
MgO	0,30	1,19
Na ₂ O	0,18	0,20
K ₂ O	2,86	4,06
loss by burning	5,40	9,96
total	100,00	99,99
quartz	32,40	

3. X-ray Diffraction Analysis (RDA) and study by scanning electronic microscopy (SEM) of fired samples with -5 μm fraction

Study of fired samples by RDA method and electronic scanning microscopy (SEM) of fraction -5 μm 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 5 μm 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 brushing for X-ray. X-ray 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 electronic scanning microscopy was also performed.

4. Results and discussion

The Figure 2 shows RDA chart of -5 μm fraction samples of Zorka brick clay fired at 600°C and transformation of clay phases into amorphous phases can be noticed on it, while the presence of mica (L), quartz (Q) and feldspar (F) is maintained. The presence of calcite (C) is also noticed. The present Fe hydroxides at this temperature give hematite (He) which appears as the new phase. The image by scanning electronic microscopy of -5 μm fraction sample of Zorka brick clay fired at 600°C is presented in Figure 3. The SEM image clearly shows that in terms of texture structure we have clear increase of porosity level with pore size of app. 10 μm , which is result of clay phase dehydration process. At this image, one can also notice effects of making out layers of the clay fraction, while mica layers are practically untouched. Based on X-ray and SEM study of -5 μm fraction sample of Zorka brick clay fired at 600°C, conclusion can be made that at this temperature, except for clay mineral dehydration process and Fe hydroxide, there are no other prominent processes for formation of new phases. The exception is formation of hematite. Considerable porosity and transformed clay phase can be stated here, with presence of still untransformed mineral phases, which gives starting material for formation of new phases at higher temperatures.

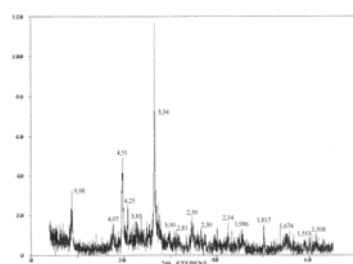


Fig. 2. RDA diagram of -5µm fraction sample of Zorka brick clay fired at 600°C

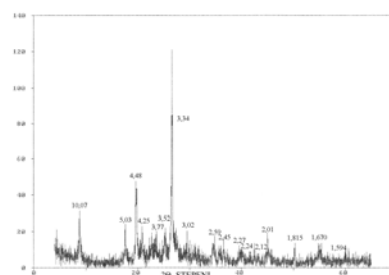


Fig. 4. RDA diagram of -5µm fraction sample of Zorka brick clay fired at 800°C

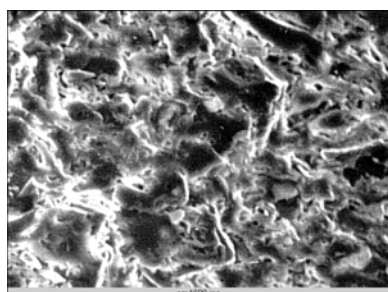


Fig. 3. SEM-image -5µm fraction sample of Zorka brick clay fired at 600°C. Magnification 3000x.

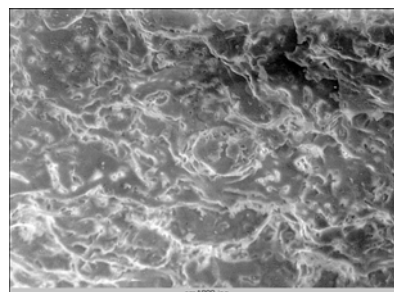


Fig. 5. SEM-image -5µm fraction sample of Zorka brick clay fired at 800°C. Magnification 2000x.

X-ray diagram of -5µm fraction sample of Zorka brick clay fired at 800°C is shown in Figure 4 while image made by scanning electronic microscopy of -5µm fraction sample of Zorka brick clay fired at 800°C is shown in Figure 5. The X-ray diagram for this sample and for this firing temperature does not show considerable differences compared to X-ray diagram obtained for the sample of the same raw material and fraction fired at 600°C – the differences are noticed in minor movement of inter-atomic distance, while the phase composition is the same as in the previous case, i.e. as in the sample fired at 600°C. On the image made by scanning electronic microscopy of -5µm fraction sample of Zorka brick clay fired at 800°C, in comparison to sample of the same raw material and fraction fired at 600°C, it is possible to clearly notice reduction of porosity level with

appearance of formation of more compact texture structure and also, it can be noticed that the pores are considerably smaller and at the same time, there is certain rounding of grain border, which is consequence of increased inter-phase border between the grain borders. On the other hand, the mica phase dips more and more into the basic mass which is made of transformed amorphous clay minerals. It can be concluded that increase of inter-phase border finally results in preparation of the whole mass for a reconstruction process which will be performed at higher temperatures, where dehydration of mica takes place as well as increase of liquid phase level and phase solubility. This is also preparation of basic mass for further phase transformation and formation of new phases.

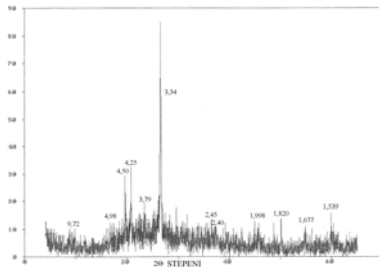


Fig. 6. RDA diagram of -5µm fraction sample of Zorka brick clay fired at 1000°C

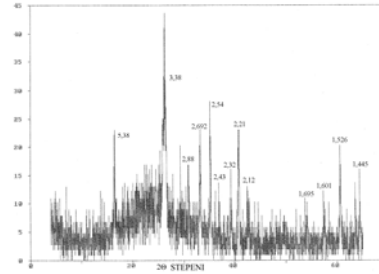


Fig. 8. RDA diagram of -5µm fraction sample of Zorka brick clay fired at 1200°C

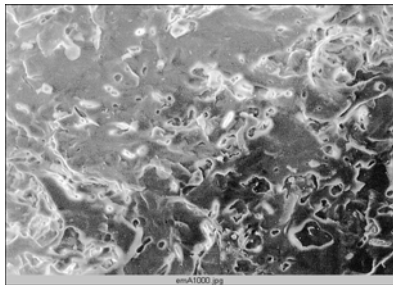


Fig. 7. SEM-image -5µm fraction sample of Zorka brick clay fired at 1000°C Magnification 3000x.

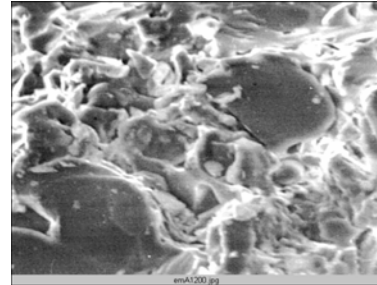


Fig. 9. SEM-image -5µm fraction sample of Zorka brick clay fired at 1200°C Magnification 2000x.

X-ray diagram of the $-5\mu\text{m}$ fraction sample of Zorka brick clay fired at 1000°C is shown on Figure 6, while on image made by scanning electronic microscopy of $-5\mu\text{m}$ fraction sample of Zorka brick clay fired at 1000°C , one can notice appearance of melilite (d-value 2.45 and 2.40) as result of reaction of carbonate dissociation with amorphous silicate phase. Reduction of mica quantity as consequence of dehydration at this temperature is noticeable. One should note that in this sample, smaller quantity of mica, however, was maintained, but with considerably disturbed basic inter-atomic distance. Reduction of basic inter-distance in mica is consequence of its incomplete dehydration, which is most probably caused by not homogenous fields of heat in certain leaves. On the image made by scanning electronic microscopy of $-5\mu\text{m}$ fraction sample of Zorka brick clay fired at 1000°C , one can notice the leaves of incompletely dehydrated mica at this temperature. The image also shows distinct relict remaining of mica which is not completely dehydrated as well as basic mass where melilite aggregates can be slightly noticed with feldspar of orthoclase and albite composition. At the places where relict remainings are incompletely dehydrated mica, somewhat bigger pores can be noticed. It should be stated that, in comparison to lower temperatures, this sample at this temperature has more compact texture-structural characteristics.

X-ray diagram of $-5\mu\text{m}$ fraction sample of Zorka brick clay fired at 1200°C is shown on Figure 8, while the image made by scanning electronic microscopy of $-5\mu\text{m}$ fraction sample of Zorka brick clay fired at 1200°C is shown on Figure 9. X-ray diagram of this sample is characterized by presence of quartz, mullite, melilite, hematite and relict remaining of feldspar as well as by presence of glassy phase which gives distinct halo effect on the diagram. The image made by scanning electronic microscopy of $-5\mu\text{m}$ fraction sample of Zorka brick clay fired at 1200°C also shows presence of irregular mullite and melilite aggregates as well as rounded quartz grains. The presence of glassy phase is also noticed, which fills the space between mullite and melilite aggregates. The porosity is lower in this sample compared to previous case just because of presence of the glassy phase which fills the interspace between mullite and melilite.

It is most probable that formation of mullite and melilite is made via glassy phase, i.e. solution which is made by assimilation of aluminium-silicon complexes of clay mineral dehydration and feldspar melting, in the first place of orthoclase. As far as feldspar melting is concerned, special

attention has to be paid to diffusion of alkali metals. In this case, it is possible to assume that alkali metals present special catalysts, i.e. mineralizers for mullite aggregate growth. In process of orthoclase heating, formation of mullite is noticed in numerous experiments.

5. Conclusion

Zorka brick clay at firing temperature of 600°C shows presence of distinct porosity with clay mineral dehydration process as well as formation of hematite as a new phase due to present iron hydroxide, while mica remains untransformed at this temperature. At temperature of 800°C, rounding of grain borders takes place and mica phase into the basic mass which is made of transformed amorphous clay minerals. At 1000°C, appearance of melilite can be noticed, while reduction of mica quantity is noticeable due to hydration at this temperature. It can be also stated here that porosity with appearance of glassy phase is present here.

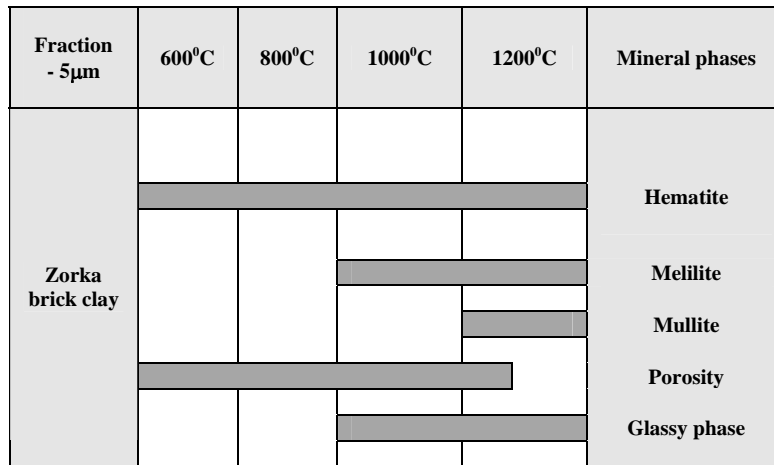


Figure 10. Survey of mineral phase depending on firing temperature of -5µm fraction sample of Zorka brick clay (indicative).

At firing temperature of 1200°C, presence of glassy phase which fills space within the present mullite and melilite aggregate is noticeable. Presence of hematite is also noticed here, as well as presence of relict

remaining of feldspar. Porosity still exists, but at lower level compared to the one stated during the study of sample from the same raw material fired at previous temperature, which is consequence of considerably more distinct presence of glassy phase in this case.

The Figure 10. gives illustration of mineral phases, depending on the firing temperature, of $-5\mu\text{m}$ fraction sample of Zorka brick clay.

6. References

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