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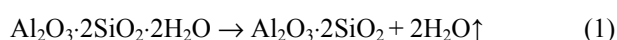
THERMAL TREATMENT OF KAOLIN CLAY TO OBTAIN METAKAOLIN

The metakaolin was produced by thermal treatment (calcination) of the starting high-quality kaolin clay from Serbia. The optimal calcination parameters, for which nearly complete dehydroxylation of the material was achieved, are: temperature 650 °C and heating time of 90 min. The conversion of the kaolinite to metakaolinite was confirmed by XRD and IR analyses of the starting and thermally treated kaolin samples. The pozzolanic activity was determined by Chapelle test. The obtained value 0.65 g Ca(OH)₂/g of metakaolin indicates that produced metakaolin may be used as supplementary cementitious material.

Development of construction materials which offers technical and environmental benefits is the main challenge of the new millennium. One of such materials is metakaolin (MK), pozzolanic addition, which is classified as a new generation of supplementary cementitious material. Supplementary cementitious materials (SCMs) are finely ground solid materials that are used to replace part of the clinker in a cement or cement in a concrete mixture. Use of metakaolin in cement-based systems, provides, beside technical [1,2], significant environmental benefits [3]. Metakaolin is unique in that it is not the by-product of an industrial process nor is it entirely natural; it is derived from a naturally occurring mineral, and is manufactured specifically for cementing applications. Metakaolin is usually produced by thermal treatment, *i.e.*, calcination of kaolin clays within a definite temperature range.

Serbia has high-quality kaolin clay deposits at Arandjelovac and Kolubara basin, and thus good potential to produce metakaolin from them.

The main process important for production high reactivity pozzolana from kaolin clay is calcination. The heating process drives off water from the mineral kaolinite (Al₂O₃·2SiO₂·2H₂O), the main constituent of kaolin clay, and collapses the material structure, resulting in an amorphous aluminosilicate (Al₂O₃·2SiO₂), metakaolinite. The process is known as dehydroxylation [4], and may be presented by simple equation:



The thermal transformation of kaolinite, which has been the subject of a large number of investigations [5–8], has shown that the heating parameters such as temperature, heating rate and time, as well as cooling parameters (cooling rate and ambient conditions), significantly influence the dehydroxylation process.

The major quantitative criterion for evaluating the performance of kaolinite by thermal treatment is a degree of the dehydroxylation, D_{tg} [9]:

$$D_{\text{tg}} = 1 - (M/M_{\text{max}}) \quad (2)$$

where M and M_{max} are residual and maximum sample mass loss, respectively. The dehydroxylation of pure kaolinite (39.5% Al₂O₃, 46.5% SiO₂ and 14% H₂O) in ambient atmosphere results in mass loss of about 14% and $D_{\text{tg}} = 1$, which corresponds to mass in bound hydroxyl ions in kaolinite.

The development of pozzolanic properties in fired clays mainly depends on nature and abundance of clay minerals in raw materials, on calcination conditions and on the fineness of the final product [10–12]. The calcination temperature producing the reactive state is usually in the range of 600–800 °C, and plays a central role in the reactivity of the resulting MK product. On prolonged heating, recrystallization and mullite (3Al₂O₃·2SiO₂) formation take place resulting in the decline of material reactivity.

The main characteristic of produced metakaolin, for the use in cement based systems, is its pozzolanic activity, which is defined as ability of material to react with calcium hydroxide in the presence of water to form compounds that have cementitious properties. Pozzolanic activity may be determined by direct [13–15] and indirect methods [16]. Direct methods are based on the measurement of the amount of lime reacted, which is determined by instrumental techniques such as thermogravimetry (TG), differential thermal analysis (DTA), X-ray diffraction (XRD) and calorimetric analysis. Indirect methods are based on the strength development occurring with reaction time. The values of pozzolanic activity indicate how good and effective pozzolan is.

The goal of this study is to determine optimal calcination parameters for obtaining metakaolin from domestic high-quality kaolin clay, for the use as supplementary cementitious material.

EXPERIMENTAL

Properties of the starting clay

Our previous study [17] showed that starting clay is high quality kaolin clay, with kaolinite content of about 80% and loss of ignition (LOI) on the temperature 950±25 °C of 12.33%. Kaolin clay was collected from the location Vrbica (Arandjelovac basin). Repre-

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sentative 5-kg samples of kaolin clay were taken from the initial materials using the quartering method. Before being characterized, the samples were dried to less than 0.5% moisture content, crushed and milled (to the particle size of less than 43 μm).

Chemical composition, determined by silicate method, and physical characteristics such as specific gravity, γ_{sr} , specific surface area, S_p , and fineness, R (given as residue on the sieve), determined according to standards SRPS EN 196-3 and SRPS EN 196-6, are given in the Table 1.

Table 1. Chemical composition and physical characteristics of the starting clay

Component	Content, mass%
SiO ₂	48.00
Al ₂ O ₃	31.75
Fe ₂ O ₃	4.38
CaO	1.00
MgO	0.48
Na ₂ O	0.16
K ₂ O	1.50
LOI	12.33
Physical characteristics	
γ_{sr} , g/cm ³	2.60
S_p , cm ² /g	9180
R , % (sieve, 0.043 μm)	4.90

Applied experimental techniques

Mineralogical composition of the starting and thermally treated clays was determined using a Siemens D5000 diffractometer (CuK α radiation, Ni filter).

Thermal behavior of the starting clay was investigated using a Netzsch STA 409EP instrument. The sample was heated from 20 to 1000 °C at a constant rate of 10 °C/min in air.

In order to confirm the characteristic bands of kaolinite in raw sample and the absence of these bands in thermally treated samples, a FTIR spectrophotometer, Nicolet 6700 Thermo Scientific, was used.

The pozzolanic activity of the thermally treated samples (metakaolin) was evaluated according to Chappelle test [18]. Metakaolin of a mass of 1 g was mixed with 1 g Ca(OH)₂ and 200 mL boiled water. The suspension was subsequently boiled for 16 h and the free Ca(OH)₂ was determined by means of sucrose extraction and titration with HCl solution.

Calcination/dehydroxylation procedure

Samples of about 50 g were heat treated in the laboratory furnace at different temperatures (550, 600, 650 and 700 °C) and at different heating times (30, 60, 90, 120, 150 and 180 min). After heating, the samples were "quenched" to room temperature at ambient conditions to avoid crystallization of amorphous metakaolin.

The weight of the samples before and after the thermal treatment was measured in order to determine weight loss during calcinations process.

RESULTS AND DISCUSSION

Thermal behavior of the starting clay is presented in the Figure 1. The main changes revealed by TG and DTA analysis are as follows [14]. At temperatures below about 200 °C release of water absorbed in pores and on the surfaces occurs. Between 200 and 450 °C, mass

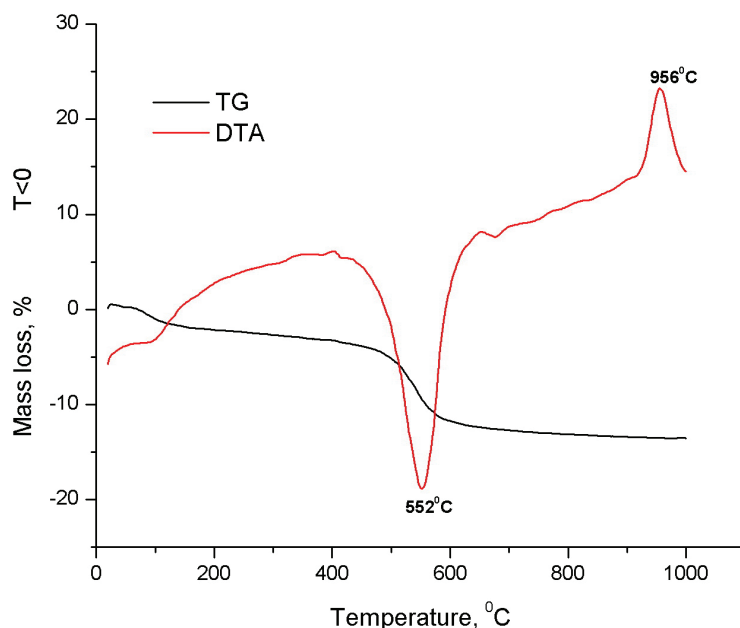


Figure 1. DTA/TG curve of the starting clay.

loss attributed to the pre-dehydration process takes place, as a result of the reorganization in the octahedral layer. In the temperature range 450–650 °C, dehydroxylation of kaolinite and formation of metakaolinite takes place, while at about 1000 °C, mullite was formed, as indicated by an exothermic peak. The observed endothermic peak with a maximum at 552 °C may be attributed to dehydroxylation process.

In order to obtain optimal calcination parameters, the clay was subjected to thermal treatment at different heating temperatures and times. The mass loss of starting clay for given calcinations parameters is given in Table 2.

As can be seen, for calcination temperatures of 550, 600 and 650 °C, mass loss increases up to 90 min, while prolonged heating has a negligible effect on the mass loss. For all applied heating times at temperature 700 °C obtained values for mass loss are nearly the same $\approx 12\%$. It is evident that at calcination temperature 650 °C and heating time 90 min, mass loss is almost identical with the values obtained at 700 °C. If we take economic factors into consideration, the optimal parameters for calcination are temperature 650 °C and heating time of 90 min.

Using mass loss values during calcination, and LOI obtained by chemical analysis (M_{\max}), the degree of dehydroxylation calculated by Eq. (2) are presented in Figure 2.

As can be seen, nearly complete dehydroxylation was achieved after 90 min for temperature of 650 and 700 °C, for which the degree of dehydroxylation, D_{tg} , is 0.97.

In order to confirm disappearance of kaolinite peaks, after thermal treatment, the XRD patterns of starting and calcined clay were compared. The results are presented in Figure 3. It is evident (Figure 3a) that the major mineral constituents of the starting clay are kaolinite and quartz. The results of XRD measurements of the calcined clays, selected on the base on their degree of dehydroxylation, are given in Figures 3b–3d. After thermal treatment of clays at temperatures 600, 650 and 700 °C and heating time 90 min, characteristic peaks for kaolinite (2θ 12.41, 20.21 and 25.49°) [19] disappear, while peaks assigned to quartz (2θ 21.22 and 27.45°) remains unchanged.

Besides XRD measurements, IR spectroscopy was applied to confirm kaolinite transformation during calcination. IR spectra obtained for starting clay and ther-

Table 2. Mass loss (%) of kaolin clay for different calcination temperatures and times

Heating time, min	Temperature, °C			
	550	600	650	700
15	–	–	10.72	11.90
30	9.26	10.56	11.22	12.00
60	10.49	11.42	11.73	12.05
90	11.11	11.80	12.00	12.07
120	11.24	11.80	12.03	12.15
150	11.33	11.74	11.92	12.11
180	11.51	11.76	–	–

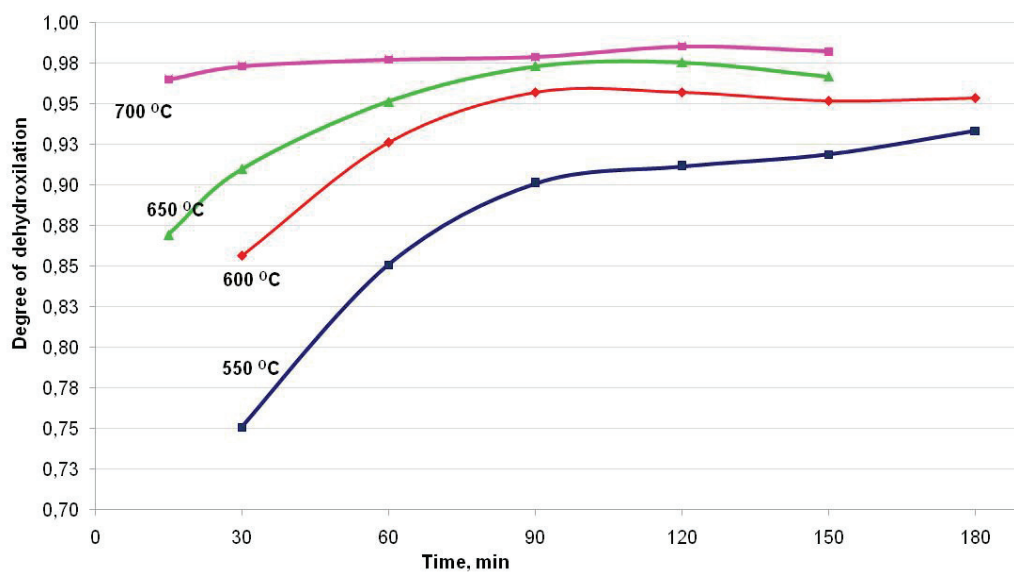


Figure 2. Dependence of degree of the dehydroxylation, D_{tg} , on calcination time for different temperatures of thermal treatment.

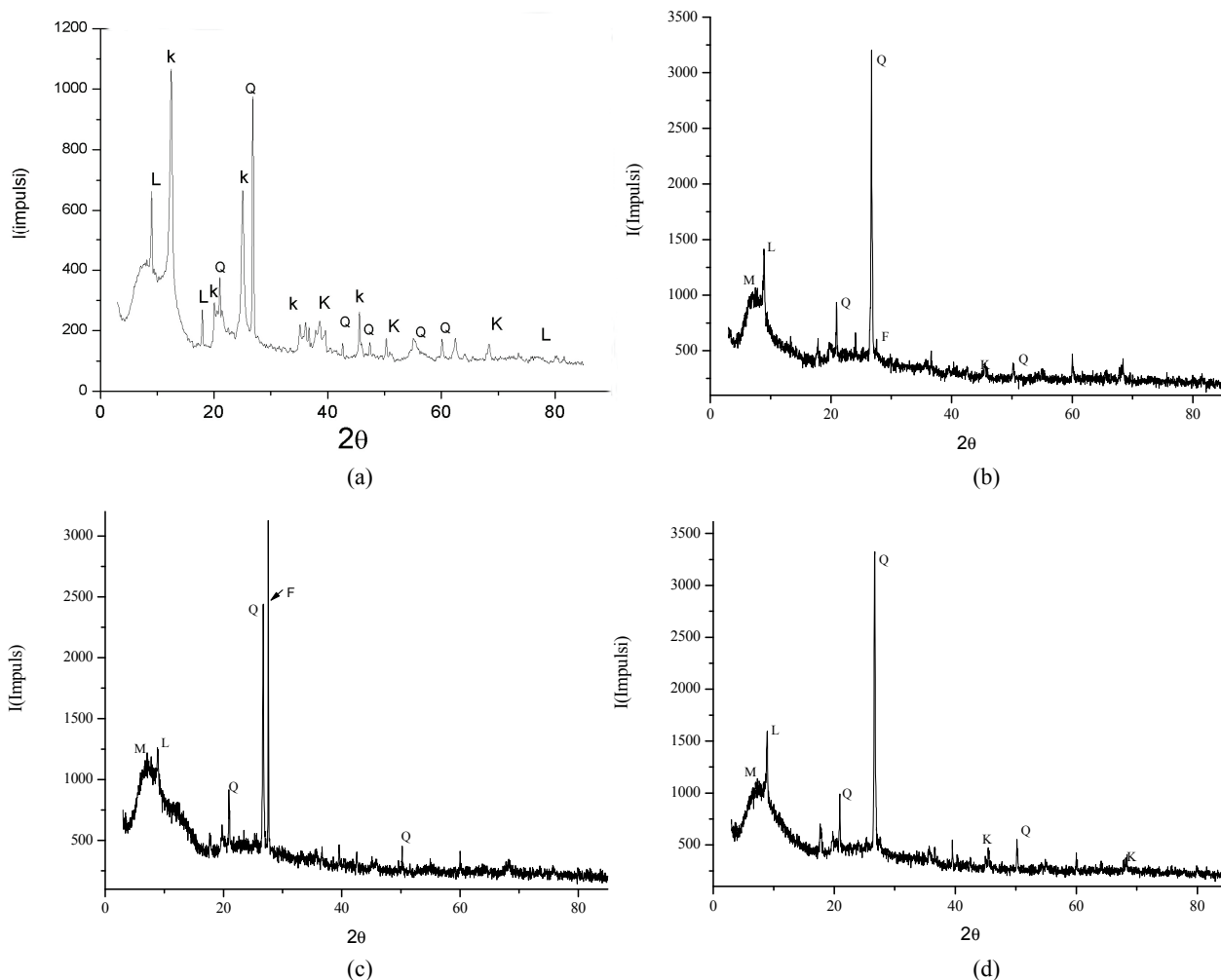


Figure 3. XRD Patterns of starting kaolin clay (a) and thermally treated (calcined) at 600 °C for 90 min (b); at 650 °C for 90 min (c) and at 700 °C for 60 min (d). K – kaolinite ($Al_2Si_2O_5(OH)_4$), Q – quartz (SiO_2), L – mica ($AlSi_2O_6(OH)_2$), F – feldspar ($(K,Na)Si_3O_8$), M – montmorillonite ($(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$).

thermally treated samples are presented in Figure 4. The results of IR spectroscopy of starting clay (Figure 4a) show the characteristic bands of kaolinite [20,21]: OH^- at 3700, 3650, 3620 cm^{-1} ; $Al-OH$ at 913 cm^{-1} ; $Si-O$ at 1032, 1008, 469 cm^{-1} and $Si-O-Al^{VI}$ at 538 cm^{-1} .

Absence of the detectable $Al-O-H$ bands at 913 cm^{-1} , and the doublet at 3700 and 3620 cm^{-1} , is evident from Figure 4b–4d. Absence of the band at 539 and 913 cm^{-1} and the appearance of a new band at 800 cm^{-1} can be related to the change from octahedral coordination of Al^{3+} in kaolinite to tetrahedral coordination in metakaolinite. The bands at 1100 and 1200 cm^{-1} are assigned to amorphous SiO_2 .

For the optimal calcination parameters (temperature 650 °C and heating time 90 min) pozzolanic activity is 0.65 g $Ca(OH)_2/g$ of metakaolin. The obtained value is in agreement with the results obtained by other authors (values from 0,55 to 0,82 g $Ca(OH)_2/g$ of metakaolin) [14].

CONCLUSION

Metakaolin, pozzolanic additive, may be obtained by calcination of kaolin clay. The optimal conditions of the thermal treatment are: calcination temperature of 650 °C and heating time of 90 min. Calcination results in dehydroxylation degree of 0.97. The produced metakaolin has pozzolanic activity 0.65 g $Ca(OH)_2 / g$ of metakaolin.

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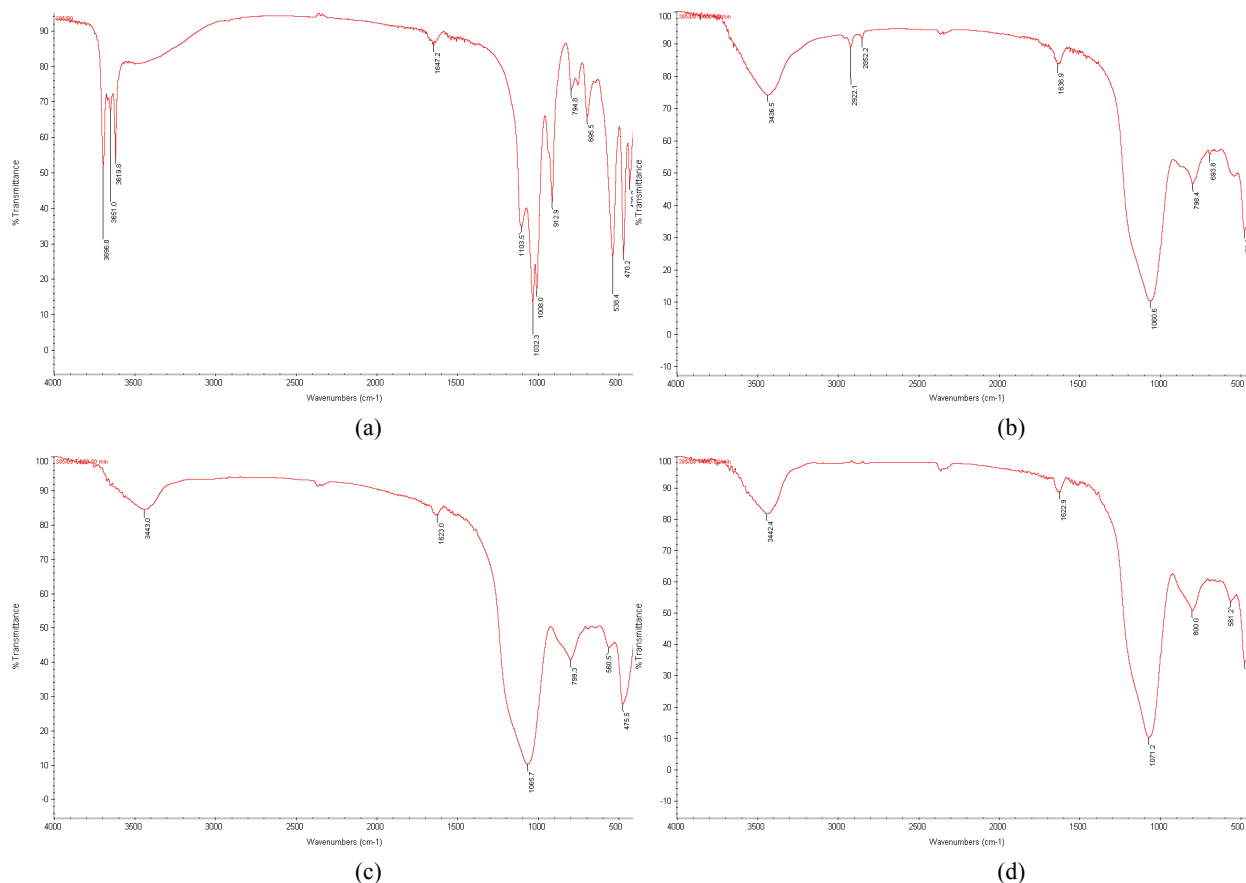


Figure 4. IR spectra of starting kaolin clay (a) and thermally treated (calcined) at 550 °C for 90 min (b); at 600 °C for 90 min (c) and at 650 °C for 90 min (d).

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IZVOD

DOBIJANJE METAKAOLINA TERMIČKIM TRETMANOM KAOLINSKE GLINE

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(Naučni rad)

U radu su prikazani rezultati istraživanja dobijanja metakaolina termičkim tretmanom domaće kaolinske gline. Polazna sirovina je bila kaolinska glina sa ležišta Vrbica (Arandjelovački basen), čiji je sadržaj kaolinita oko 80% i gubitak žarenjem 12,33%. Diferencijalnom termičkom analizom (DTA/TGA) utvrđeno je da do dehidroksilacije i transformacije kaolinita u metakaolinit dolazi u opsegu temperature 450–700 °C. Proces kalcinacije je praćen termičkim tretmanom kaolinske gline u laboratorijskim uslovima na temperaturama 550, 600, 650 i 700 °C, različito vreme: 15, 30, 60, 90, 120, 150 i 180 min. Kao glavni kvantitativni kriterijum za ocenu ponašanja kaolinita u procesu kalcinacije, korišćen je stepen dehidroksilacije materijala, D_{tg} . Optimalni parametri procesa kalcinacije, pri kojima je postignut stepen dehidroksilacije 0,97, jesu: temperatura 650 °C i vreme zagrevanja 90 min. Transformacije kaolinita u metakaolinit potvrđene su rendgenskom strukturnom analizom i IR spektroskopijom polazne gline i termički tretiranih gline. Na difraktogramima termički tretiranih gline nisu uočeni karakteristični pikovi kaolinita, dok IR spektri pokazuju odsustvo karakterističnih veza kaolinita. Pucolanska aktivnost metakaolina, određena direktnom metodom, pri optimalnim uslovima kalcinacije iznosi 0,65 g Ca(OH)₂ / g metakaolina. Na osnovu ovih istraživanja može se zaključiti da je kaolinska glina sa nalazišta Vrbica pogodna za proizvodnju metakaolina, odgovarajuće pucolanske aktivnosti, a koji se može primenjivati u svojstvu dopunskog cementnog materijala u sistemima na bazi cementa.

Ključne reči: Kaolin • Metakaolin • Kalcinacija • Dehidroksilacija
Key words: Kaolin • Metakaolin • Calcination • Dehydroxylation