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Original scientific paper

## Mechanochemical treatment of Serbian kaolin clay to obtain a highly reactive pozzolana

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**Abstract:** Mechanochemical treatment of Serbian kaolin clay was performed in a planetary ball mill using two different milling media, hardened steel or zirconia vials and balls. The samples obtained after various milling times were characterized by particle size laser diffraction (PSLD), X-ray diffraction (XRD), differential scanning calorimetry/thermogravimetry (DTA/TGA) and Fourier-transform infrared (FTIR) analyses. The mechanochemical treatment induced amorphization of the kaolinite phase accompanied by dehydroxylation. It was found that for given milling parameters, amorphization mainly occurred in the milling period up to 15 min, and was completed after about 30 min of milling for both employed milling media. The pozzolanic activities were determined by the Chapelle method. Milling in the hardened steel milling medium had no significant influence on pozzolanic activity, even though there was accumulated iron contamination. For both milling media, a pozzolanic activity of 0.79 was obtained for the samples milled for 15 min and it remained almost unchanged with prolonged milling. The determined pozzolanic activity values were similar to those of commercial metakaolinite or metakaolinite obtained by calcination of the same clay, thereby, indicating that highly reactive pozzolana could be obtained by mechanochemical treatment of Serbian kaoline clay.

**Keywords:** kaolin clay; kaolinite; metakaolinite; mechanochemical treatment; pozzolana.

### INTRODUCTION

Kaoline clays are important industrial materials, used in engineering and construction applications, ceramic processing, environmental remediation and in many other miscellaneous applications.<sup>1</sup> There is an ongoing interest in the utilization of kaolin clays as raw materials for the manufacture of metakaolin

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(MK), a dehydroxylated form of the clay mineral kaolinite, as a pozzolanic additive for cement and concrete. MK usage can be found in many aspects of obtaining concrete and can have beneficial effects on the ultimate compressive strength, permeability and chemical durability, as well as economic and ecological advantages.<sup>2</sup> Bearing this in mind, as well as the lack of traditional pozzolanic materials (*e.g.*, fly ash and silica fume), great effort has been given to improving the technical characteristics MK as well as its production using kaolin clay as the raw material.<sup>3–5</sup>

Metakaolinite ( $\text{Al}_2\text{Si}_2\text{O}_7$ ) is an X-ray amorphous reactive aluminosilicate, commercially obtained by heat treatment of kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) clay.<sup>6,7</sup> The heat treatment involves the use of fossil fuels that produce  $\text{CO}_2$  and other gases ( $\text{NO}_x$  and  $\text{SO}_x$  types), all of which are air pollutants. Recently, there has been an effort to reduce the emissions of greenhouse gases, and to develop processes less aggressive to the environment. One of these processes is mechanical treatment, widely applied for the modification and synthesis of various classes of materials.<sup>8–10</sup> The mechanochemical treatment of kaolinite has also been reported in several papers.<sup>11–21</sup>

In Serbia, there are several high-quality kaolin clay deposits: the Arandelovac Basin, the Kolubara Basin, and the Vranje and Kriva Reka Basin. Certain quantities of the kaolin clays from these deposits are used in the ceramic industry and for the production of refractory materials. In order to find other possible applications, a process of metakaolin production by heat treatment (calcination) of Serbian kaolin clay was developed.<sup>22</sup> Good pozzolanic activity, as well as mechanical and physical characteristics of the cements with the addition of metakaolin produced by calcination and subsequent milling,<sup>23</sup> gave substantial reason to try to produce reactive pozzolana with a process less aggressive to the environment, *i.e.*, mechanochemical treatment.

Although a lot of work on milled kaolinite has been reported in recent years,<sup>11–21</sup> there seem to be only one report on the pozzolanic activity of amorphous kaolinite obtained by mechanochemical treatment.<sup>19</sup> Furthermore, it should be born in mind that the mineral composition of natural kaolin clays from different locations usually differ remarkably, thus influencing the physical and chemical properties of produced kaolinite.

In this work, the results of mechanochemical treatment of Serbian kaolin clay, performed using either hardened steel or zirconia vial and balls as the milling media, are presented. The investigations were focused on how milling influences the pozzolanic activity and whether contamination arising from balls and vial debris affects the properties of the final product. The results obtained enable a better understanding of kaolinite preparation by milling and its properties as a pozzolanic additive.

## EXPERIMENTAL

*Material*

Kaolin clay from the Arandelovac Basin in Serbia was used for mechanochemical treatment. Before characterization and mechanochemical treatment, clay was dried to less than 0.5 % moisture content, crushed and then ground in ball mill for 10 min (sample denoted as 0 h).

The chemical composition of the starting clay expressed in mass % of oxides was SiO<sub>2</sub>, 48.00; Al<sub>2</sub>O<sub>3</sub>, 31.75; Fe<sub>2</sub>O<sub>3</sub>, 4.38; CaO, 1.00; MgO, 0.48; Na<sub>2</sub>O, 0.16; K<sub>2</sub>O, 1.50 and loss on ignition 12.33 %. The main physical characteristics of the starting clay were given previously.<sup>23</sup>

The semi quantitative estimation, namely chemical analysis in combination with X-ray diffraction (XRD) analysis was used to determine the kaolinite and quartz contents of 80 and 10.6 mass %, respectively.

*Milling procedure*

The powders were milled without any additives (dry milling) in a planetary ball mill – Fritsch Pulverisette 5 – using either hardened steel 500 cm<sup>3</sup> vials and 13.4 mm diameter balls or 500 cm<sup>3</sup> zirconia vials (yttrium oxide added ZrO<sub>2</sub>) vials and 10.0 mm diameter balls, in an air atmosphere. The masses of the powders were 25 and 20 g for milling in the hardened steel and zirconia vials, respectively, giving a balls-to-powder mass ratio of about 25 for both sets of milling. The angular velocity of the supported (basic) disc, measured by a tachometer, varied between 340 and 350 rpm (35.6 and 36.7 rad s<sup>-1</sup>) throughout the milling. Thus, the milling parameters were such that the same milling intensity may be expected for both milling media.<sup>24,25</sup> Due to contamination arising from ball and vial debris, the color of the powders milled in the hardened steel vials gradually darkened from almost white to black. Prolonged milling up to 5 h was deliberately performed in order to investigate the possible effect of contamination on the properties of the clay prepared by mechanochemical treatment. Thus, chemical analysis of the powder milled for 5 h revealed an iron contamination of 5.6 %. Milling in zirconia was performed for up to 2 h of milling. Determination of the ZrO<sub>2</sub> contamination by chemical analysis was not performed but since the XRD analysis did not reveal a ZrO<sub>2</sub> phase, it should be no greater than a few percent.

*Experimental techniques*

The particle size distribution was measured by laser particle size analyzer on Mastersizer 2000 (Malvern Instruments Ltd., UK), which covers the particle size range of 0.02–2000 μm.

The X-ray powder diffraction data were collected on a Philips PW1710 diffractometer using Cu-Kα graphite-monochromatized radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the  $2\theta$  range 4–65° (step-length: 0.02°  $2\theta$ , scan time: 5 s).

The thermal behavior of the starting clay and powders milled for 15 and 30 min and for 1 and 2 h was investigated from room temperature up to 1100 °C using an SDT Q600 simultaneous DSC–TGA instrument (TA Instruments) with a heating of 20 °C min<sup>-1</sup> under a dynamic (100 cm<sup>3</sup> min<sup>-1</sup>) N<sub>2</sub> atmosphere.

The Fourier-transform infrared (FTIR) spectra were recorded using Nicolet 6700 Thermo Scientific spectrometer. Measurements were conducted in the wave number range 4000–400 cm<sup>-1</sup>, with 4 cm<sup>-1</sup> resolution.

The pozzolanic activity was evaluated according to the Chapelle test.<sup>26</sup> Kaolinite clay of a mass of 1 g was mixed with 1 g Ca(OH)<sub>2</sub> and 200 cm<sup>3</sup> boiling water. The suspension was subsequently boiled for 16 h and the free Ca(OH)<sub>2</sub> was determined by the means of sucrose extraction and titration with HCl solution.

## RESULTS AND DISCUSSION

*Particle size distribution*

Particle size measurements revealed that mechanochemical treatment using either hardened steel or zirconia vials and balls induced only a moderate powder change compared to the kaolin clay pre-milled for 10 min (Fig. 1). Mean particle size slightly increased from 9.85 to 11.34  $\mu\text{m}$  after 15 min, because of particle agglomeration, and remained almost unchanged for milling times up to 30 min in the hardened steel vial. Such an observation is in an agreement with previously reported results.<sup>15</sup> Particle size reduction of the fraction of coarse powder particle size could also be noticed. The powder behaved in a similar manner during milling in the zirconia vial.

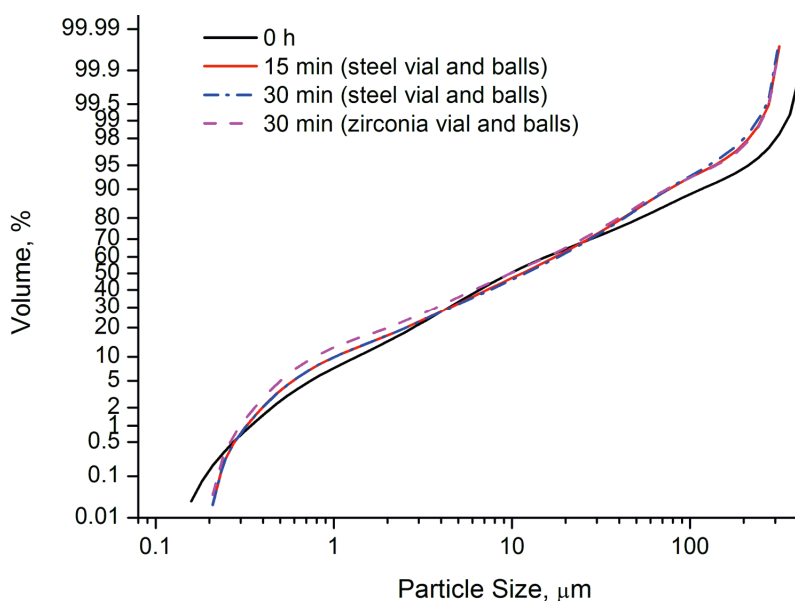


Fig. 1. Particle size distribution of the kaolin clay pre-milled for 10 min (0 h) and milled for 15 and 30 min using hardened steel balls and vial and milled for 30 min using zirconia balls and vial.

*XRD structural analysis*

The XRD patterns of the starting clay and samples milled for various milling times, for both milling media, are presented in Figs. 2 and 3. XRD analysis of the starting clay identifies kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) by basal reflections at about  $2\theta$  12.4, 20.0, 21.0 and 25.0° (JCPDS card No. 89-6538), quartz at  $2\theta$  20.9 and 26.7° (JSPDS card No. 89-8934) and mica at  $2\theta$  8.9 and 17.9° (JCPDS card No. 88-0791). In the XRD pattern of the sample milled for 15 min, the peaks of kaolinite had almost vanished (or can hardly be resolved) as the result of deterioration of

the kaolinite structure. The loss of peak intensity at  $2\theta$  12.4° suggests breaking of the bonds between the kaolinite layers (001).<sup>15</sup> Mechanochemical treatment induces dehydroxylation, and the consequential transformation of kaolinite to a very disordered (amorphous) structure. It was already demonstrated that during milling, the kaolinite phase becomes gradually distorted and amorphous.<sup>13–16</sup> For the thermally induced transformation of kaolinite to metakaolin, a molecular dynamic study showed that the loss of crystallinity was governed by the loss of hydroxyl groups at the surface of the inter-layer spacing and the migration of the aluminum into the vacant sites.<sup>7</sup>

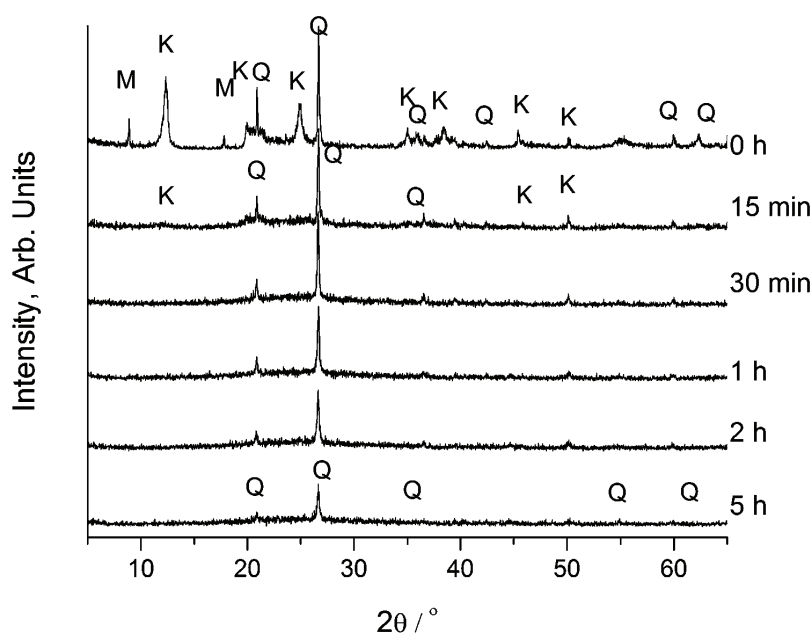


Fig. 2. XRD Patterns of the kaolin clay milled for various milling times using hardened steel balls and vial (K – kaolinite, Q – quartz, M – mica).

The XRD patterns of the samples milled for longer milling times (30 min, 1, 2 and 5 h) are similar (Figs. 2 and 3), indicating that with prolonged milling structural changes occurred very slowly. The XRD patterns suggest that the quartz phase was not altered because the position of peaks at  $2\theta$  21.2 and 27.4° remained almost unchanged. However, their intensities gradually decreased, perhaps as the result of very slow dissolution of quartz into the disordered (amorphous) matrix. XRD analysis of mechanically treated samples during either hardened steel or zirconia milling medium indicated fast deterioration of the kaolinite structure during milling, mainly within the first 15 min. The results obtained in this study are consistent with previous investigations.<sup>11–19</sup>

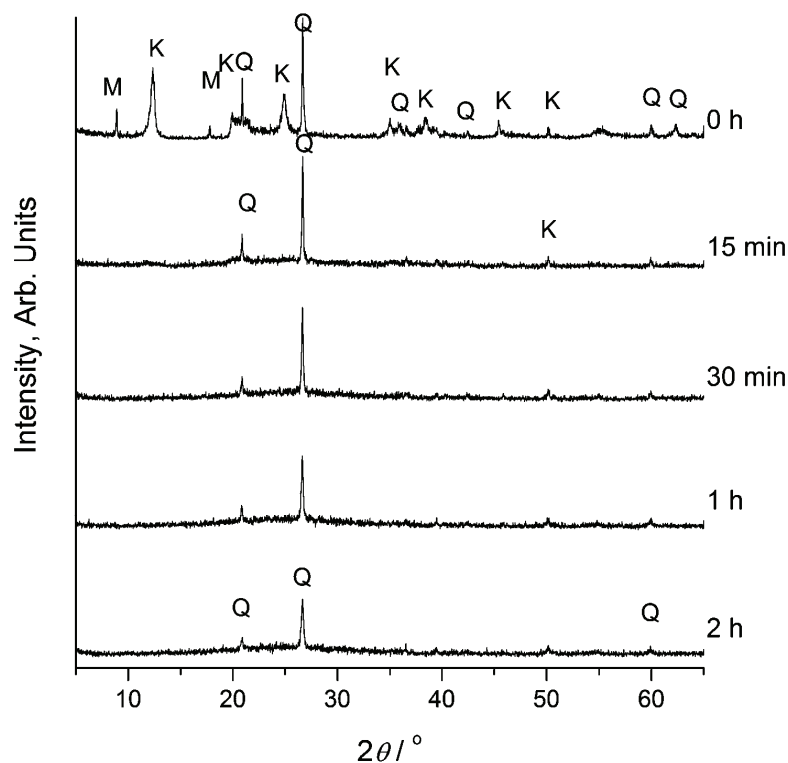


Fig. 3. XRD Patterns of the kaolin clay milled for various milling times using zirconia balls and vial (K – kaolinite, Q – quartz, M – mica).

The observation that almost identical results were obtained in both milling media suggests that specific energy dose defined as cumulative mechanical energy transferred to the powder during milling time is responsible for the kinetics and final phase formation, in spite of different milling parameters such as impact energy and frequency.<sup>27</sup>

#### *DTA/TGA thermal analysis*

Thermal analysis of the samples milled for various milling times further supports the XRD findings. On the DTA curve (Fig. 4a) of the pre-milled clay (milling time 0 h), two heat effects could be identified. A well-developed endothermic peak at a temperature of about 511 °C, assigned to the process of dehydroxylation, was accompanied with a weight loss of about 12 % during heating up to temperatures of about 800 °C (Fig. 4b). At higher temperatures, the exothermic heat effect at about 982 °C could be assigned to the crystallization of spinel and/or mullite phases.<sup>12</sup>

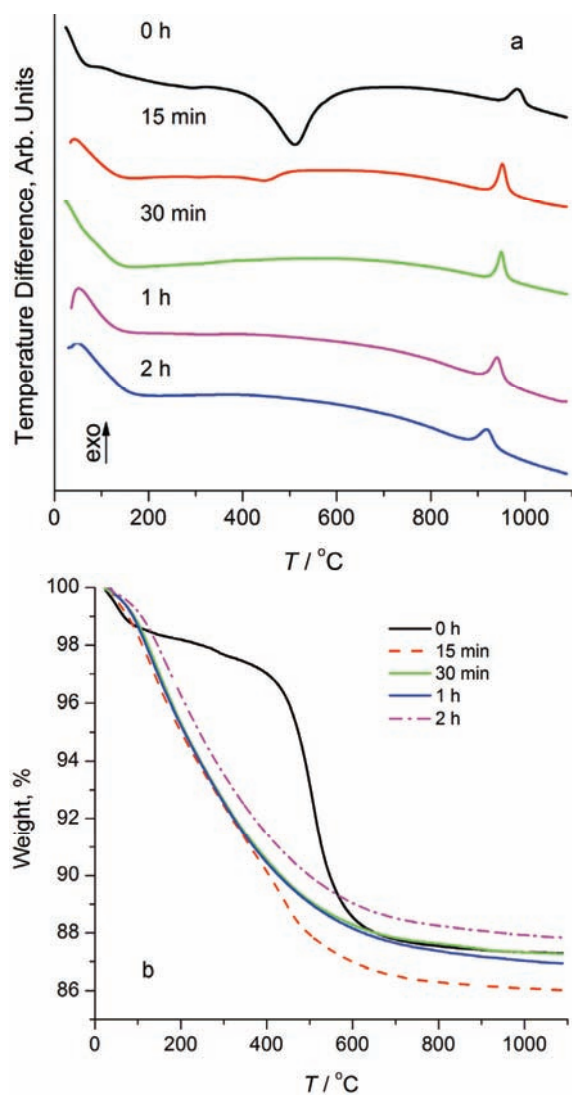


Fig. 4. DTA (a) and TGA (b) curves of the kaolin clay milled for various milling times using hardened steel balls and vial.

For the sample milled for 15 min, the endothermic heat effect had almost disappeared, indicating that mechanochemical treatment induced breaking of O–H bonds. It should also be noted that this peak was shifted to a lower temperature of about 460 °C. Thus, mechanochemical treatment through the generation of lattice defects decreased the dehydroxylation temperature by about 50 °C. For prolonged milling times, such a heat effect could not be detected, implying that the process of dehydroxylation was completed in up to about 30 min of milling. The exothermic peak shifted to lower temperatures with milling time (from 982 to 920 °C for 0 and 2 h, respectively), which is in agreement with

previously reported results.<sup>12</sup> DTA results (Fig. 4b) show that water release was facilitated in the milled samples in comparison to the unmilled sample.

DTA/TGA curves of the samples milled in the zirconia-milling medium along with metakaolinite sample prepared by heat treatment (calcination) of the kaoline clay at 650 °C for 90 min,<sup>22</sup> are given in Fig. 5. As can be seen, milled samples exhibited a very similar thermal behavior to that milled in hardened steel, suggesting contamination had no significant effect on the dehydroxylation process. Therefore, the weight loss between 100 and 300 °C (Figure 4b and 5b) may be attributed to the liberation of coordinated water, which is formed from

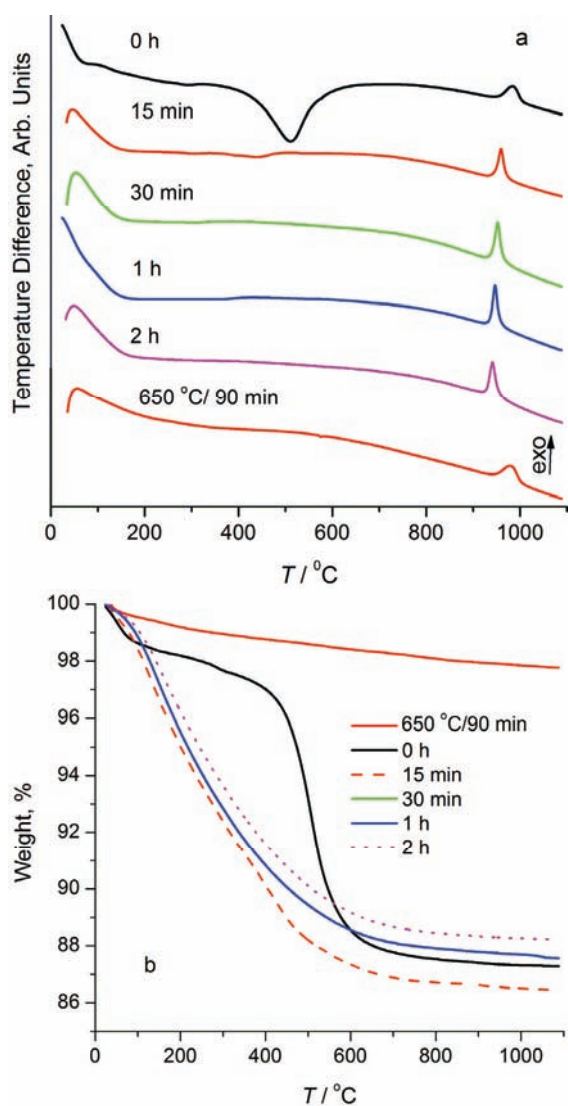


Fig. 5. DTA (a) and TGA (b) curves of the kaolin clay milled for various milling times using zirconia steel balls and vial.



the OH groups because of mechanochemical dehydroxylation of kaolinite. The difference in the thermal behavior of amorphous kaolinite and of metakaolinite is obvious from Fig. 5. The metakaolinite sample was characterized by the absence of a dehydroxylation heat effect (Fig. 5a), while the TGA measurement did not reveal any significant weight loss (Fig. 5b).

#### *Infrared analysis*

The FTIR spectra of the pre-milled kaolin clay and those of the kaolin clay milled for 15 and 30 min, and 1 and 2 h in the zirconia-milling medium are shown in Fig. 6. The characteristic bands at 3697, 3651 and 3620  $\text{cm}^{-1}$ , assigned to SiO–H stretching vibrations, were markedly decreased in intensity in the spectra of the mechanochemically treated samples, indicating the scission of O–H bonds. The appearance of a broad band at 3443  $\text{cm}^{-1}$  may be assigned to the hydroxyl vibrations of interlayer and adsorbed water.<sup>11,19–21,28</sup> The very weak but detectable bands at 3697 and 3624  $\text{cm}^{-1}$  indicate that after 30 min of milling, some OH groups still remained bonded between the adjacent kaolin layers, evidencing that some residual kaolinite phase still existed. However, on prolonging the milling time up to 1 h, these bands completely disappeared, implying completion of the dehydroxylation process. No significant difference could be observed between samples milled for 1 and 2 h.

FTIR spectra of the samples milled in hardened steel milling media (not given) exhibited almost identical features as presented in Fig. 6.

#### *Pozzolanic activity*

Determination of pozzolanic activity, and in particular lime reactivity, of various materials is essential for their efficient application in cement and concrete. The influence of milling time of the kaolin clay on the pozzolanic activity is given in Table I. It is evident that after 15 min of milling, the pozzolanic activity reached its highest value of 0.79 g  $\text{Ca}(\text{OH})_2$  per g pozzolana. Prolonged milling slightly decreased the pozzolanic activity. The values obtained were similar to those of metakaolinite obtained by calcination<sup>22</sup> and subsequent milling<sup>23</sup> for the same kaolinite clay, as well as commercial metakaolinite, implying that mechanochemical treatment could be applied to produce highly reactive pozzolana.

It is known that the lime reactivity of a pozzolanic material depends on its particle size and surface area as well as its mineralogical composition.<sup>29</sup> High reactivity pozzolans are those that contain large proportions of amorphous aluminosilicates, have particles of small average mean diameter and relatively high specific surface. Therefore, taking the structural changes of the starting clay during milling into the account, it could be presumed that amorphization of the studied kaolinite was the main factor responsible for the obtained pozzolanic activity.

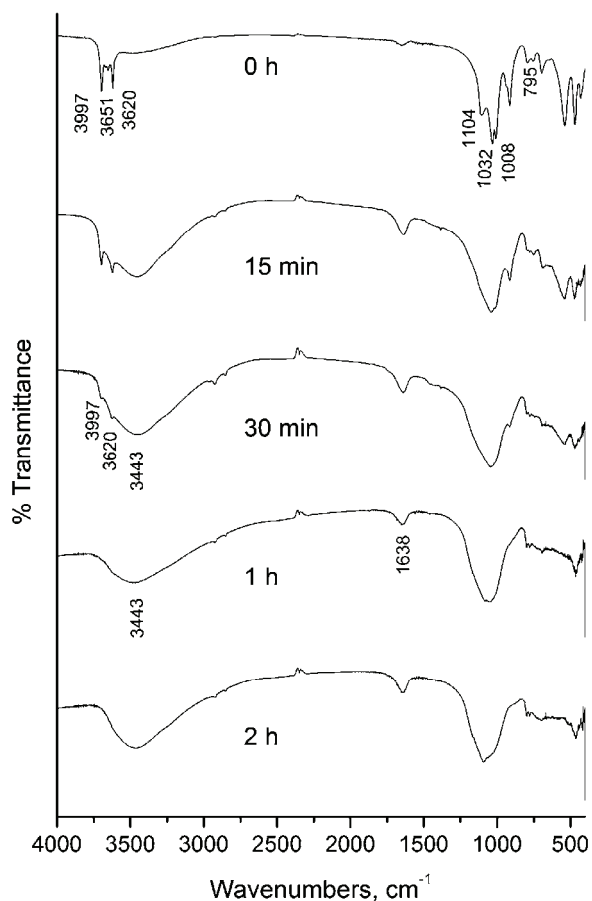


Fig. 6. FTIR Spectra of a kaolin clay pre-milled for 10 min (0 h) and milled for various milling times using zirconia steel balls and vial.

TABLE I. Pozzolanic activity of the kaolinite clay milled for various milling times in either hardened steel or zirconia milling medium (balls and vial), and obtained by calcination and subsequent milling in comparison to commercial metakaolinite

Milling time	Pozzolanic activity, g Ca(OH) <sub>2</sub> per g pozzolana	
	Hardened steel	Zirconia
0 h (pre-milled for 10 min)		0.59
15 min	0.79	0.79
30 min	0.75	0.74
2 h	–	0.73
5 h	0.76	–
Metakaolinite obtained by calcination <sup>21</sup>		0.65
Metakaolinite obtained by calcination and subsequent milling <sup>22</sup>		0.76
Commercial metakaolinite		0.78

## CONCLUSIONS

The results obtained in this study show the feasibility of obtaining highly reactive pozzolan by mechanochemical treatment. The results could be summarized as follows:

Milling in a hardened steel or zirconia medium has no significant effect on the pozzolanic activity beyond a milling time of 15 min.

Contamination arising from ball and vial debris during milling in hardened steel also had significant effect on the pozzolanic activity.

Milling of the pre-milled clay induces only moderate changes in the particle size distribution.

XRD and DTA/TGA analyses of mechanically treated clays indicated a fast deterioration of the kaolinite structure (amorphization) occurred mainly within the first 15 min.

The absence of a signal at  $913\text{ cm}^{-1}$  arising from Al–O–H bonds in the IR spectra of milled samples confirmed mechanochemical dehydroxylation and transformation to amorphous kaolinite.

Milling for more than 30 min was unnecessary, as further milling has no significant effects on the characteristics of the pozzolan.

In conclusion, mechanochemical treatment instead of the heat treatment could be employed for the production of pozzolan with the same activity.

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## ИЗВОД

РЕАКТИВНИ ПУЦОЛАН ДОБИЈЕН МЕХАНОХЕМИЈСКИМ ТРЕТМАНОМ  
ДОМАЋЕ КАОЛИНСКЕ ГЛИНЕ

АЛЕКСАНДРА МИТРОВИЋ<sup>1</sup> и МИОДРАГ ЗДУЛИЋ<sup>2</sup>

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Домаћа каолинска глина је механохемијски третирана у планетарном млину коришћењем челичних или  $\text{ZrO}_2$  посуда и куглица. Узорци добијени после различитих времена млевења испитивани су рендгенском структурном (XRD) и диференцијално термичком и термогравиметријском (DTA/TGA) анализом, инфрацрвеном спектроскопијом са Фуријеовом трансформацијом (FTIR), као и ласерском дифракцијом расподеле величине честица ((PSLD)). Механохемијски третман проузрокује аморфизацију каолинске фазе праћену дехидроксијацијом. Нађено је да је аморфизација интензивна током почетних 15 min млевења, а да је готово у потпуности завршена након 30 min млевења. Пуцоланска активност је одређивана *Chapelle* методом. Млевење у челичним посудама у трајању од 5 h нема битног утицаја на пуцоланску активност, иако је током млевења дошло до запрљања праха гвожђем. Вредност пуцоланске активности од 0,79 добијана је за узорак млевен 15 min у челичним као и за онај млевен у  $\text{ZrO}_2$  посудама, и остаје го-

тово непромењена за дужа времена млевења. Одређене пуцоланске активности блиске су вредностима за комерцијални метакаолинит, као и за метакаолинит добијен калци-нацијом каолинске глине истог хемијског састава. На основу овога, може се закључити да је механохемијски третман погодна метода за добијање рекативног пуцолана.

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