

PARTIAL REPLACEMENT OF CEMENT WITH CALCINED CLAYS FROM CENTRAL BOSNIA

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ABSTRACT

Two clays from deposits located in the region of Central Bosnia, and kaolin obtained from a local spark plug and technical ceramics factory were calcined at 800, 900, and 1000 °C. The pozzolanic activity of calcined raw materials was determined using the P test. Calcined clay from the deposit Bilalovac showed slightly better reactivity compared to calcined clay from the deposit Klokoti, and in both clays, the reactivity increased with increasing calcination temperature. Calcined kaolin was more reactive than clays and the highest reactivity was achieved when calcined at 800 °C. The strengths of mortars in which 20 % of cement was replaced with calcined raw materials showed the same trend of behavior as in the P test. Partial replacement of cement with calcined clays lead to a slight decrease in the strength of cement mortar, and the best results were obtained with clays calcined at 1000 °C.

1. INTRODUCTION

Each tonne of cement releases a little under a tonne of carbon dioxide, approximately half of that produced by the calcination of limestone. The remainder results from fuel used for the production of electrical energy needed for the grinding process and for fuel used in firing the materials [1]. The potential for atmospheric carbon reduction in the cement industry is through the resource-efficient use of pozzolanic materials. The possibilities of using new materials that can replace part of the clinker in Portland cement or part of the cement in concrete mixes are being intensively researched [2-9]. New materials should reduce energy consumption and gas emissions, and improve the characteristics of cement, mortar, and concrete to which they are added. The replacement materials have in common that they, in finely divided form, can react with $\text{Ca}(\text{OH})_2$ in the presence of water to form a variety of excess cement phases.

Traditionally, the market for industrial pozzolans has been dominated by pulverised fuel ash (PFA) and blast furnace slag (BFS). In the long term, these resources are in decline; most of the world's production of suitable blast furnace slag and fly ash are already destined for use in the cement industry and it would seem timely to consider other options for blended cement production. Calcined clays, even those of somewhat lower quality (with a lower kaolinite content), are regarded as an appropriate alternative to the existing replacement materials [10-16].

This paper presents the results of research into the possibility of using domestic raw materials as substitute cement materials. For this purpose, two readily available local clays from central Bosnia were examined. Kaolin obtained from the "Enker" Factory in Tešanj was tested as a material for comparison.

2. EXPERIMENTAL WORK

2.1 Raw materials

The used raw materials were:

- clay from the exploitation field of the former factory of refractory materials from Busovača from the locality Klokoti - designated as clay A,
- clay from the area of the municipality of Kiseljak from the locality of Bilalovac - designated as clay B,
- kaolin from the "Enker" factory in Tešanj - designated as kaolin K.

Particle size distribution analysis of raw materials was carried out using the laser method on a Malvern Mastersizer 2000 particle size analyzer.

Loss on ignition was determined gravimetrically after heating up samples at 900 °C. The content of SiO₂ was also determined gravimetrically, while the content of Al₂O₃, Fe₂O₃, TiO₂, CaO, MgO, K₂O, Na₂O, and MnO after dissolving with acids was determined on a Perkin Elmer atomic absorption spectrometer.

The mineralogical composition of clays and kaolin was determined using simultaneous DTA and TGA on the instrument Netzsch STA 409 CD and XRD analysis. During DTA and TGA tests, samples were heated in a nitrogen atmosphere from room temperature to 1000 °C at a heating rate of 10 °C/min. X-ray diffraction analysis was performed on a Bruker D8 ENDEAVOR XRD diffractometer.

2.2. Preparation of samples

Dried raw clays A and B and kaolin K and water were used to prepare the samples for calcination. The dried raw clays were first sieved on a 1 mm sieve. 300 g of each of the clays and kaolin were weighed on an analytical balance. 65 ml of water was added to clay A, 75 ml to clay B, and 99 ml to kaolin K. The pastes were mixed by hand and shaped into cylinders with a height of 40 mm and a diameter of 33 mm. The prepared cylinders were air-dried for one day and then placed into the furnace for calcination according to the firing regime shown in Figure 1. After calcination, the samples were marked with a letter corresponding to the raw material (A, B, and K) and a number corresponding to the calcination temperature (800, 900, and 1000 °C).

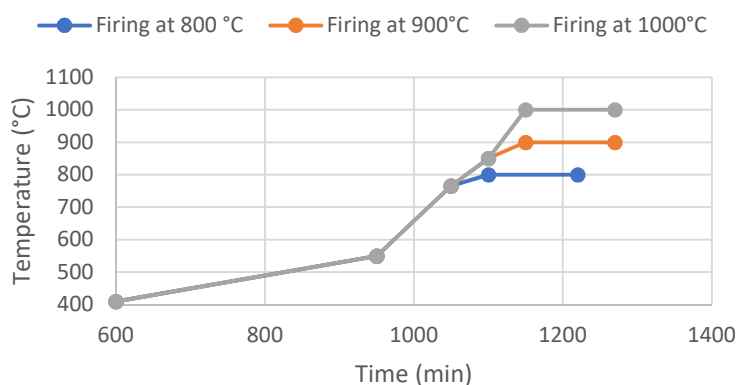


Figure 1. The regime for the firing of samples

The calcined samples were ground in a mill manufactured by "Herzog", power 400 W, dimensions 1.0 x 0.60 x 0.70 m, weight 80 kg, capacity 200 g. The grinding bodies were eccentric rings, and the grinding time was 30 seconds. Mineralogical analysis of ground calcined samples was performed using X-ray diffraction analysis on an XRD diffractometer Bruker D8 ENDEAVOR.

2.3 Determination of the pozzolanic reactivity of clays and kaolin

In this work, two methods were used for assessing the pozzolanic reactivity of clay and kaolin:

- portlandite ($\text{Ca}(\text{OH})_2$) consumption test - marked as P test
- test of changes in cement mortar strength with 20 % replacement of cement with calcined clays and kaolin.

A pozzolanic reaction takes place between the cementitious replacement material and $\text{Ca}(\text{OH})_2$ in the presence of free water to form C-S-H, C-A-H, or C-A-S-H phases. Since it is complicated and difficult to directly measure the amount of replacement cementitious material consumed in the pozzolanic reaction, an alternative method that is usually accepted to study the progress of the reaction is to determine the consumption of $\text{Ca}(\text{OH})_2$. For a sample containing unreacted $\text{Ca}(\text{OH})_2$, the mass loss due to dehydration of $\text{Ca}(\text{OH})_2$ within a certain temperature range can be measured by TG analysis. The most common temperature range in which the decomposition of portlandite ($\text{Ca}(\text{OH})_2$) occurs in the literature is around 350 to 550°C [10].

In this work, the temperature range 450 – 560 °C was used to determine mass loss via TGA under conditions of heating in a nitrogen atmosphere at a heating rate of 10 °C/min. This temperature range was chosen because the curves obtained on the device on which the test was carried out showed that within this range a reaction takes place accompanied by mass loss. In order to measure the properties of cementitious materials at a very early age, it is necessary to remove free water to stop cement hydration. Free water is replaced in the first step with an organic solvent that can be mixed with water, and in the second step, the solvent is removed by evaporation. Isopropanol was chosen as an inert solvent replacing water due to its minimal effect on the microstructure [10,17-19].

The preparation of the mixtures consisted of weighing 10 g of calcined raw materials for each separately in a plastic container and then adding 10 g of pure $\text{Ca}(\text{OH})_2$, manual mixing for 1 minute. After mixing, 20 ml of distilled water was added, and the whole mixture was stirred for another 2 minutes. After that, the plastic container was closed, labeled, and placed in a laboratory oven at 40 °C. After 7, 14, and 28 days, the containers were taken out of the oven, and a part (approximately 1/4) was taken from each sample, and placed in another plastic container into which isopropanol was poured in an amount that is approximately ten times greater than the amount of the separated sample as hydration would stop. The rest of the paste was closed again and returned to the oven until the next sampling. The samples prepared in this way were left in isopropanol for three days. After three days, isopropanol was separated by filtration, and the samples were dried in a laboratory oven with a digital thermoregulator at 60 °C to a constant mass. The samples were then subjected to DTG/TG analyses to determine the amount of unreacted portlandite. Analyses were performed on a Netzsch STA 409 instrument from room temperature to 1000 °C, with a heating rate of 10 °C/min. Samples with an initial mass of approximately 50 mg were placed in an alumina crucible. During the measurement, the furnace was purged with nitrogen flow at a rate of 40 ml/min. The analysis results were processed using Netzsch Proteus Thermal Analysis software.

Cement mortars with 20 % replacement of cement with calcined clays and kaolin were prepared and tested on compressive and flexural strength after 7, 28, and 90 days according to the standard EN 196-1.

3. RESULTS AND DISCUSSION

3.1 Characteristics of raw materials

The particle size distribution of the starting raw materials is shown in Table 1. Kaolin K consists of smaller particles compared to clays, while clay B has the largest particles and

the differences in granulation between clays A and B are smaller compared to the differences between kaolin and clays. This confirms the assumption that kaolin K has the most clay minerals and the least impurities.

Table 1. Particle size of clays A and B and kaolin K

Sample	Particle diameter [μm]		
	d(0.1)	d(0.5)	d(0.9)
Clay A	3.481	12.261	33.479
Clay B	4.225	15.678	44.076
Kaolin K	2.468	8.870	21.528

Table 2. Chemical composition of raw materials

Component	Chemical composition (wt. %)		
	Clay A	Clay B	Kaolin K
SiO ₂	70.7	63.60	48.90
Al ₂ O ₃	17.8	22.3	37.81
Fe ₂ O ₃	1.40	2.04	1.20
CaO	1.27	0.95	/
TiO ₂	0.003	0.006	0.00
MgO	0.48	0.76	0.00
MnO	0.008	0.008	/
K ₂ O	3.65	4.66	2.20
Na ₂ O	0.30	0.50	/
ZnO	0.019	0.016	/
LOI	4.11	4.98	12.17

Table 2 shows results related to the chemical analysis of raw materials. Chemical analysis shows that all three tested raw materials have the most SiO₂ and Al₂O₃, which is typical for clays and indicates the presence of clay minerals and quartz and possibly feldspar. Kaolin K has the most Al₂O₃, which is assumed to have the most kaolinite, and clay A the least. On the other hand, clay A has the most SiO₂, so it is assumed that this clay has the most quartz compared to the other two raw materials. Potassium is in third place in terms of representation in raw materials, and

it comes from illite and muscovite or from potassium feldspar, and it is most abundant in clay B. In fourth place is iron, which most likely comes from illite. The amount of CaO in the clays is insignificant, which indicates that the clays do not contain calcium compounds, primarily carbonate. Kaolin K has the highest loss on annealing, which again indicates a large amount of kaolinite, while in the case of clays A and B this loss is much smaller and does not differ much, indicating a smaller amount of clay minerals compared to kaolin K. Figure 2 shows differential thermal analyses and thermogravimetric analyses of raw materials. Thermal tests on a DTA/TG device confirmed the presence of kaolinite (endothermic peaks at 585, 586 and 608 °C on DTA curves, as well as a significant mass loss on the TG curves in that temperature regions), illite and/or muscovite (mass loss at around 900 °C) in all three raw materials. Again, it was confirmed that the most kaolinite has kaolin K, where an exothermic peak can be clearly observed at 1010 °C, which confirms the transformation of kaolinite into a new crystalline phase at high temperatures. Such a peak, but of much lower intensity, is also observed on the DTA curve of clay A at 996 °C. The mass losses determined by this method are in good agreement with the annealing losses during chemical analysis.

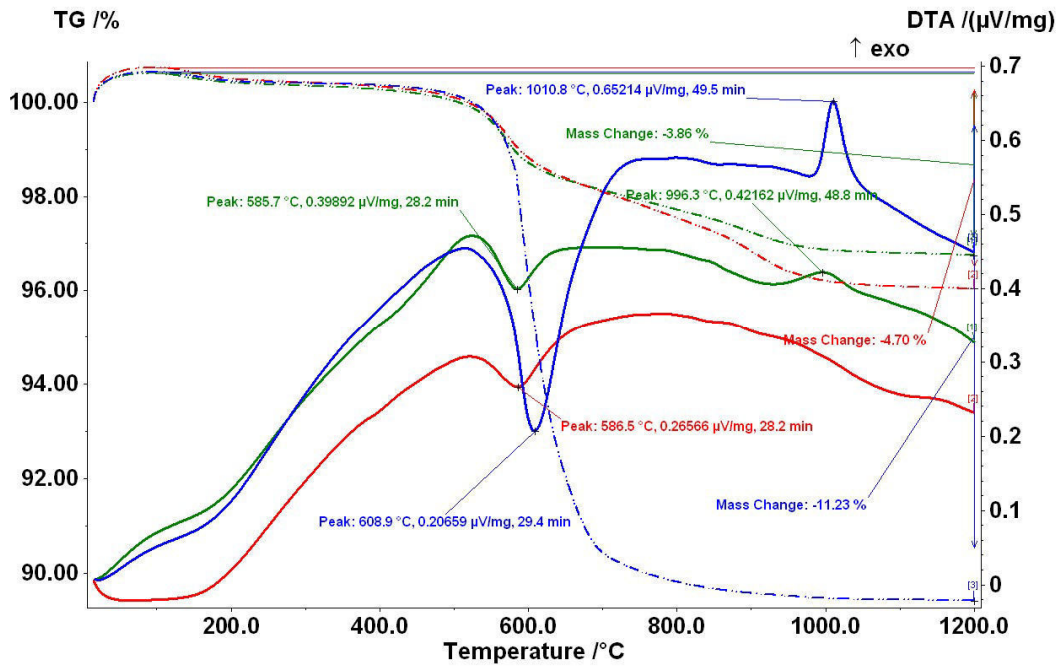


Figure 2. DTA/TG analysis of raw materials (green – clay A, red – clay B, blue – kaolin K)

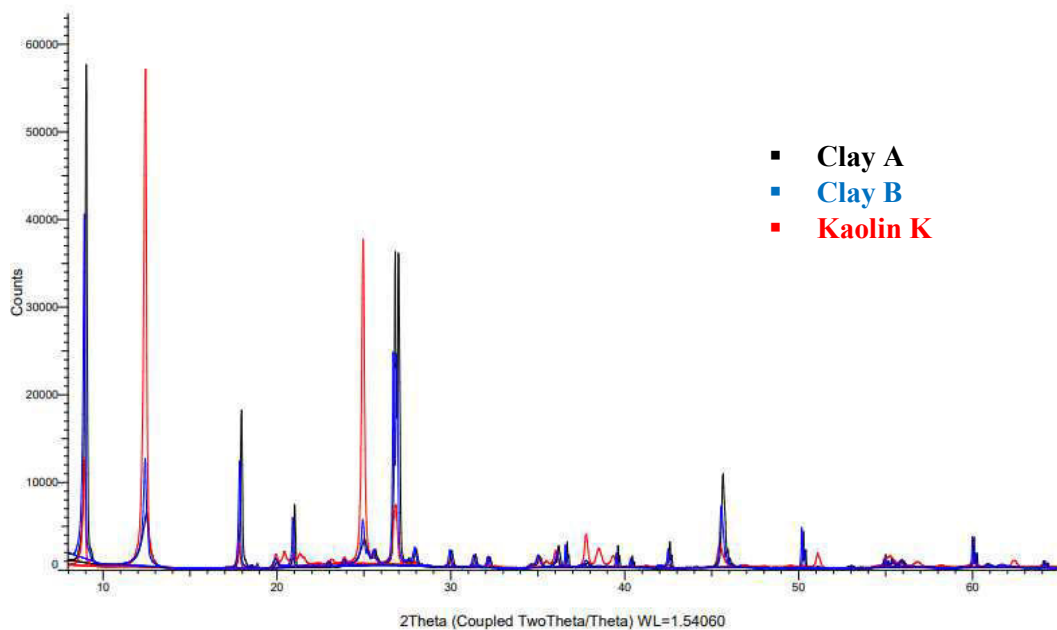


Figure 3. X-ray spectrum of raw materials

Figure 3 shows the diffractograms of the starting materials which show that they contain mainly muscovite and/or illite, kaolinite, and quartz. The diagrams also show that clay A has the most quartz, which agrees with the chemical analysis that shows that clay A has the largest amount of SiO₂. A higher amount of kaolinite is observed in clay B compared to clay A, which again coincides with the chemical analysis that shows a higher amount of Al₂O₃ in clay B compared to clay A. The amount of muscovite and/or illite is the highest in clay A, which does not match with the amount of K₂O in the chemical analysis where clay

B has the highest amount of K_2O , so it was to be expected that it also has the most illite and/or muscovite. However, there is a possibility that K_2O also comes from some other minerals, for example, feldspar whose peaks are difficult to see on an X-ray, because they often overlap with the peaks of muscovite and quartz. Kaolinite is most abundant in kaolin K, in which smaller amounts of quartz and muscovite, and/or illite are also observed.

X-rays of clays and kaolin calcined at 800 °C show peaks of muscovite and/or illite and peaks of quartz, while the peaks of kaolinite have disappeared, which means that up to this temperature the kaolinite mineral has completely decomposed in all tested raw materials. The peaks of muscovite and/or illite are of lower intensity compared to uncalcined raw materials, which indicates that their decomposition also started at a temperature lower than 800 °C.

On the X-ray images of clays and kaolin calcined at 900 °C (Figure 4), the same peaks as for clay and kaolin calcined at 800 °C are observed, but the intensity of the peaks of muscovite and/or illite is lower, which means that their decomposition has continued. In the X-ray image of kaolin calcined at 800 °C, the appearance of new peaks of low intensity is observed, which probably belong to the spinel-type phase or mullite recrystallizing from the liquid phase. Such a phase appears with clay B calcined at 900 °C, and with clay A only after calcination at 1000 °C.

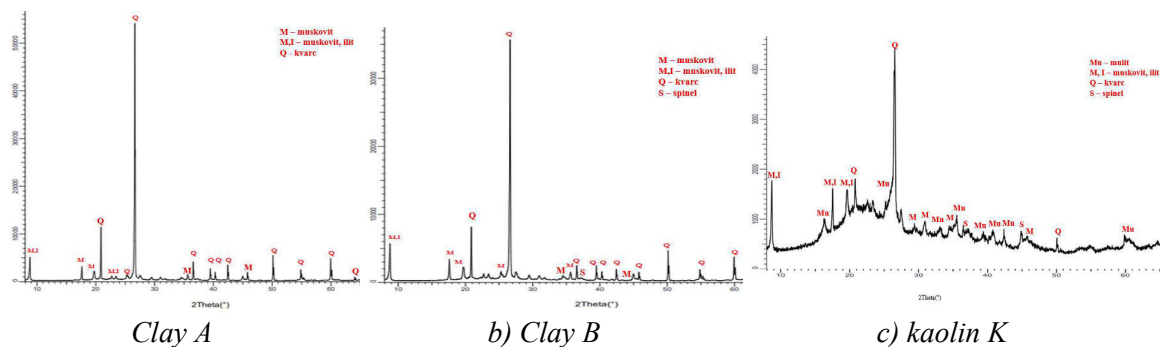


Figure 4. X-ray spectrum of raw materials calcined at 900 °C

In the case of raw materials calcined at 1000 °C, there are no more peaks of muscovite and/or illite, which means that their decomposition is complete, the peaks created by calcination at 900 °C intensify and new peaks corresponding to the spinel or mullite phase appear, especially pronounced in kaolin. Kaolin K calcined at all three temperatures shows a significantly more amorphous phase compared to calcined clays A and B.

3.2 Pozzolanic reactivity

Using the P test, the effect of different temperatures on the pozzolanic reactivity of calcined clays and kaolin was defined. Mass loss in the temperature range of 450-560 °C was determined on TG curves. The smaller this mass loss, the more portlandite was consumed in the reaction with the calcined raw materials, i.e. these calcined raw materials have a better pozzolanic reactivity.

The results (Figure 5) showed that calcined clay A and calcined clay B behave similarly. Slightly better reactivity in all test conditions is shown by calcined clay B. As the calcination temperature increases, so does the reactivity of these clays, which is probably the result of a decrease in the amount of the crystalline phase, i.e. the amount of muscovite and/or illite, and an increase in the amount of the more reactive amorphous phase.

Kaolin K calcined at 800 °C shows significantly higher reactivity compared to clays calcined at this temperature. Kaolin K calcined at 900 °C still has higher reactivity than clays calcined at this temperature, but it is less pronounced. Calcination of kaolin K at 1000

°C significantly reduces its reactivity, so that it is now less than the reactivity of clays. This is probably the result of a more pronounced crystallization of the spinel or mullite phase, and a decrease in the amount of the amorphous phase.

In all tested samples, reactivity increases with increasing reaction time. Kaolin K shows the best reactivity when calcined at 800 °C and after 28 days of holding at 40 °C, and clays A and B when calcined at 1000 °C and also after 28 days of holding at 40 °C.

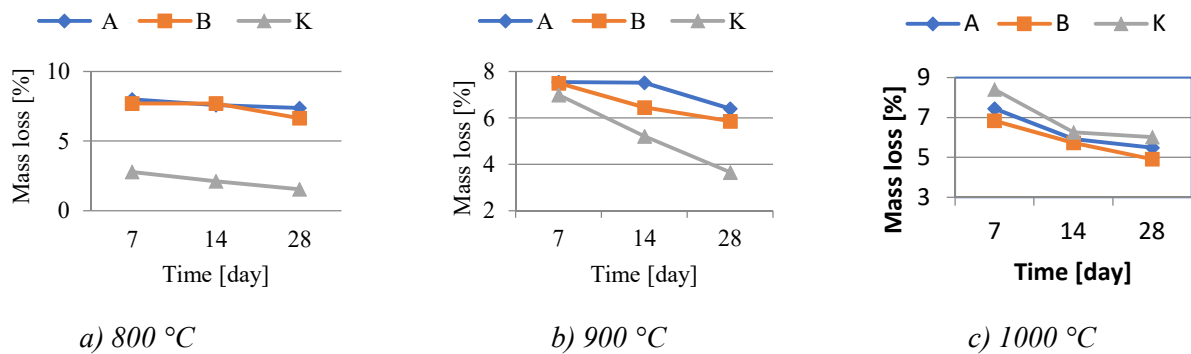


Figure 5. Results of P test

The impact of replacing cement with calcined raw materials in the amount of 20 % was tested on the flexural and compressive strength of the cement mortar. The properties of tasted mortars were also compared with those of the control Portland cement CEM I mortar. The results of this test (Figure 6 and Figure 7) show the same behaviour trend as in the P test, i.e. the materials that showed better pozzolanic reactivity in the P test show higher compressive and flexural strength. Mortars with calcined clay A behave similarly to mortars with calcined clay B. Mortars with calcined clay B have slightly higher strength. As the calcination temperature increases, the strength of mortars with these clays increases.

The compressive strengths of mortars with kaolin calcined at 800 °C are close to the strengths of mortars with CEM I 52,5 N cement, while the strengths of mortars with clays calcined at the same temperature are significantly lower. All mortars with raw materials calcined at 900 °C and 1000 °C have lower compressive strength compared to the mortar with only CEM I 52,5N cement.

According to the EN 197-1 standard, which prescribes the criteria for the physical and mechanical properties of cement, all the tested samples show appropriate values. The compressive strength of cement with the addition of kaolin calcined at 800 °C after 28 days is 56.1 MPa, which corresponds to cement class 52.5. Cement with the addition of calcined kaolin at 900 °C has a compressive strength of 44.61 MPa, which corresponds to cement class 42,5 N. Samples with the addition of calcined kaolin, clay A and clay B at 1000 °C have a compressive strength of 35.1 MPa, which corresponds to class 32.5 cements [20].

Mortars with kaolin calcined at 800 °C have higher strength compared to mortars with clays calcined at this temperature. The strengths of mortars with kaolin calcined at 900 °C are slightly higher or even almost the same in relation to the strengths of mortars with clays calcined at this temperature. Mortars with kaolin calcined at 1000 °C have less strength than mortars with clays calcined at this temperature.

The strengths of all tested samples increase with the increase in the curing time of the mortar. Of the mortars with calcined kaolin, the mortar with kaolin calcined at 800 °C and after 90 days of care has the highest strength, and of the mortar with calcined clays, clays A and B when calcined at 1000 °C and also after 90 days of care.

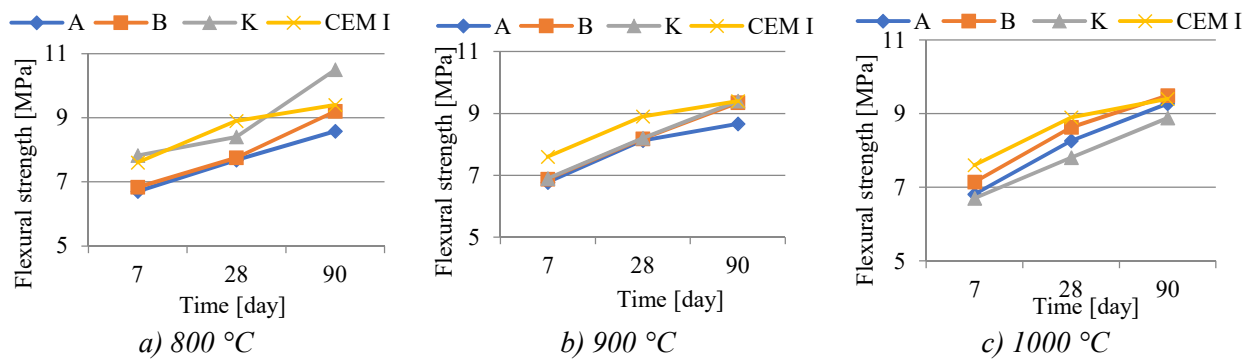


Figure 6. Flexural strength

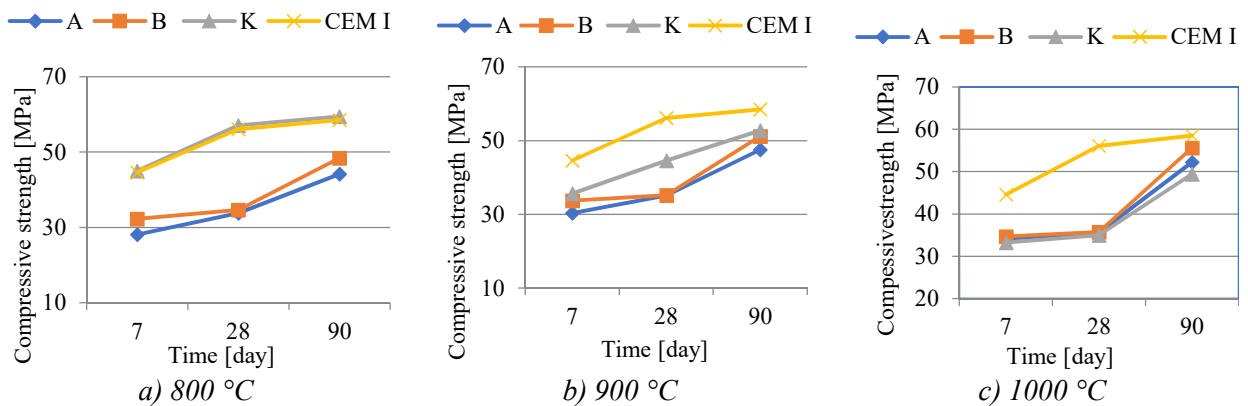


Figure 7. Compressive strength

4. CONCLUSION

Based on the presented results, the following can be concluded:

- Kaolin K consists of smaller particles compared to clays, while clay B has the largest particles and the differences in granulation between clays A and B are smaller compared to the differences between kaolin and clays. It is known that cement has higher reactivity and better mechanical properties with higher grinding fineness.
- Diffractograms of the starting materials show that they contain mainly muscovite and/or illite, kaolinite, and quartz. The diagrams also show that clay A consists mostly of quartz. That agrees with the chemical analysis that shows that clay A has the largest amount of SiO_2 . A higher amount of kaolinite is observed in clay B compared to clay A, which again coincides with the chemical analysis that shows a higher amount of Al_2O_3 in clay B compared to clay A.
- Kaolin K calcined at all three temperatures shows a significantly more amorphous phase compared to calcined clays A and B.
- Using the P test, the effect of different temperatures on the pozzolanic reactivity of calcined clays and kaolin was defined. The results showed that calcined clay A and calcined clay B behave similarly. Slightly better reactivity in all test conditions is shown by calcined clay B. As the calcination temperature increases, so does the reactivity of these clays, which is probably the result of a decrease in the amount of the crystalline phase, i.e. the amount of muscovite and/or illite, and an increase in the amount of the more reactive amorphous phase.
- The impact of replacing cement with calcined raw materials in the amount of 20 % was tested on the flexural and compressive strength of the cement mortar. The properties of tasted mortars were also compared with those of the control Portland cement CEM I

mortar. The results of this test show the same behavior trend as in the P test, i.e. the materials that showed better pozzolanic reactivity in the P test show higher compressive and flexural strength. Mortars with calcined clay A behave similarly to mortars with calcined clay B. Mortars with calcined clay B have slightly higher strength. As the calcination temperature increases, the strength of mortars with these clays increases.

- The compressive strengths of mortars with kaolin calcined at 800 °C are close to the strengths of mortars with CEM I cement, while the strengths of mortars with clays calcined at the same temperature are significantly lower.
- All the compressive strength values of the tested samples correspond to the criteria for the physical and mechanical properties of cement according to EN 197-1. The compressive strength of samples with kaolin decreases with increasing calcination temperature, which also decreases the cement class. The samples with clays A and B have approximate compressive strength values, regardless of the calcination temperature, and correspond to the cement of class 32.5.
- The strengths of all tested samples increase with the increase in the curing time of the mortar. Of the mortars with calcined kaolin, the mortar with kaolin calcined at 800 °C and after 90 days of care has the highest strength, and of the mortar with calcined clays, clays A and B when calcined at 1000 °C and also after 90 days of care.
- This research has shown that it is possible to partially replace cement with calcined clays from the area of Busovača and Kiseljak, although they lead to a slight decrease in the strength of the cement mortar. The most favorable temperature for calcination of tested clays is 1000 °C.

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